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<b>(51) International Patent Classification <sup>5</sup> :</b> <b>G03F 7/11, H01B 3/36</b> <b>C07C 42/20</b>	<b>A1</b>	<b>(11) International Publication Number:</b> <b>WO 92/11580</b> <b>(43) International Publication Date:</b> <b>9 July 1992 (09.07.92)</b>
<b>(21) International Application Number:</b> PCT/US91/09392 <b>(22) International Filing Date:</b> 11 December 1991 (11.12.91)  <b>(30) Priority data:</b> 630,118 19 December 1990 (19.12.90) US 630,107 19 December 1990 (19.12.90) US  <b>(71) Applicant:</b> ALLIED-SIGNAL INC. [US/US]; Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).  <b>(72) Inventors:</b> ZUPANCIC, Joseph, James ; 17W 338 Belmont, Bensenville, IL 60106 (US). BLAZEJ, Daniel, Charles ; 1 Grace Drive, Annandale, NJ 08801 (US). FRAENKEL, Howard, Alan ; 201H Stanton Lebanon Road, Lebanon, NJ 08833 (US).		<b>(74) Agent:</b> ROONEY, Gerard, P.; Allied-Signal Inc., Law Department (C.A. McNally), P.O. Box 2245R, Morristown, NJ 07962-2245 (US).  <b>(81) Designated States:</b> AT (European patent), BE (European patent), CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), MC (European patent), NL (European patent), SE (European patent).  <b>Published</b> <i>With international search report.</i>
<b>(54) Title:</b> PHOTODEFINABLE INTERLEVEL DIELECTRICS  <b>(57) Abstract</b>  A predetermined pattern of a dielectric polymer is formed on a substrate from either a first prepolymer which is an ether of the reaction product of a dicyclopentadiene and a phenol or a mixture of said prepolymer with a second prepolymer which is an ether of the reaction product of a dialdehyde and 3 to 4 moles of a phenol.		

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<sup>+</sup> Any designation of "SU" has effect in the Russian Federation. It is not yet known whether any such designation has effect in other States of the former Soviet Union.

PHOTODEFINABLE INTERLEVEL DIELECTRICS

The U. S. Government has rights in this invention under  
U.S. Air Force Contract F33615-89-C-5603

5 PRIOR ART

This invention relates to materials used to provide isolation of conductive layers in microelectronic circuitry. In particular, it relates to polymeric materials which can be photopolymerized so  
10 that dielectric layers can be formed where desired in multilayer structures. Such layers must be excellent insulators, have good chemical resistance and, of course, must adhere to the substrate on which they are placed.

15 Polyimides have been used for such dielectrics since they have superior temperature and chemical resistance compared to many other polymers. Literature and patents disclosing of the use of polyimides are extensively discussed in U. S. Patent  
20 4,908,096 by one of the present inventors. The disadvantages of the polyimides are discussed, namely, that they release large amounts of volatiles during curing, absorb moisture, have poor adhesion, and have a relatively high coefficient of expansion. The patent  
25 discloses and claims the use of other polymers as interlevel dielectrics having improved properties, namely, vinyl benzyl or alkyl ethers of the condensation products of dialdehydes and phenols.

The present invention relates to other  
30 polymers which have been found to provide useful interlevel dielectrics.

In U. S. 4,824,920 one of the present inventors has disclosed thermosetting resins which are vinylbenzyl ethers of the reaction product of a  
35 dicyclopentadiene with a phenol and which have application to making laminated boards for electronic applications. In U.S. Pat. No. 4,816,498 another family of oligomeric condensation products was

disclosed which differ from those just discussed in being the condensation products of dialdehydes with 3 to 4 moles of phenols. Such oligomers also are etherified to provide a mixture of vinylbenzyl and alkyl ethers. They may be used to make laminated boards for electronic applications. Such resins have been found to be useful as precursors for polymers for interlevel dielectrics, as will be seen in the discussion below.

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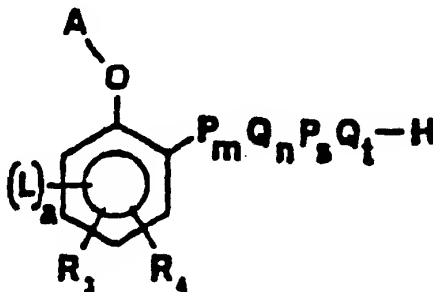
#### SUMMARY OF THE INVENTION

This invention comprises a method of forming a predetermined pattern from a polymer on a substrate and the thus-created dielectric layers which may be used in an electronic interconnect structure.

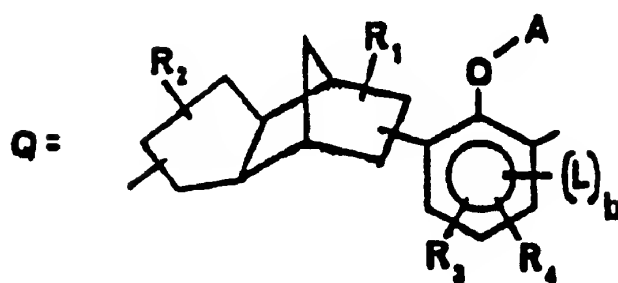
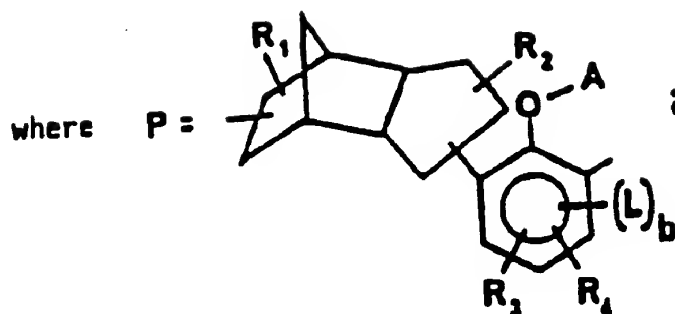
Such patterns are created by coating onto the substrate a prepolymer and then irradiating the exposed portions of a masking pattern to render the prepolymer insoluble, then selectively dissolving the non-irradiated masked portions of the coating leaving the insoluble irradiated prepolymer, and curing the irradiated prepolymer to form an infusible glassy solid in the predetermined pattern.

The prepolymer is either the first of two oligomers described below or is a mixture of both of the oligomers. One is a vinylbenzyl ether of the reaction product of a dicyclopentadiene with a phenol, the reaction product having the formula

30




35



with  $R_1, R_2 = H$  or alkyl of 1-10 carbon atoms;

$R_3 = \text{methyl}$ ;

$R_4 = H$ ;

$A = H, -CH_2-$  , an alkyl moiety containing 1

to 10 carbon atoms,  $R_5$  a cycloalkyl moiety having 5 to 10 carbon atoms, or benzyl, subject to the constraint that at least 50% of all A's are the vinyl benzyl moiety;

$L = Br$  or  $Cl$ ;

$a = 0, 1, \text{ or } 2$ ;

$b = 0 \text{ or } 1$ ;

$m, n, s,$  and  $t$  are 0 or an integer, and  $m+n+s+t=z$  is an integer from 1-10; and

$R_5 = H, \text{ an alkyl moiety of 1-10 carbon atoms, a halogen or alkoxy moiety, or a monovalent aromatic}$

radical. In a preferred embodiment, 70% of A's are vinyl benzyl and the remaining A's are propyl.

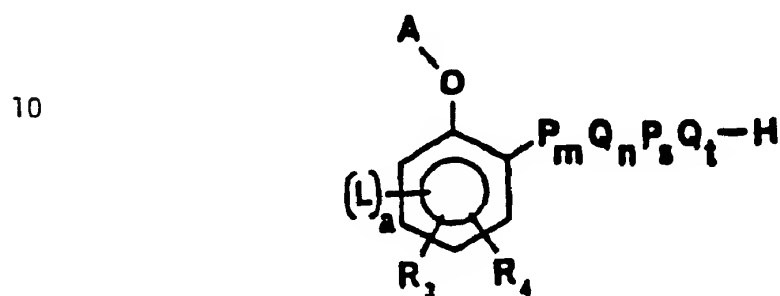
The second oligomer is an ether of the oligomeric condensation product of (a) 1 molar proportion of a dialdehyde and (b) from about 3 to about 4 molar proportions of a phenol; where the dialdehyde is selected from the group consisting of  $\text{OHC}(\text{CH}_2)_n\text{CHO}$ , where  $n = 0$  or an integer from 1 to 6, cyclopentanedialdehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, hexahydrophthalaldehyde, cycloheptanedialdehyde, hexahydroisophthalaldehyde, hexahydroterephthalaldehyde, and cyclooctanedialdehyde; where the phenol has the structure  $\text{R}_1\text{C}_6\text{H}_4\text{OH}$  and where  $\text{R}_1$  is hydrogen or an alkyl group containing from 1 to about 10 carbon atoms; and where the phenol residue of said oligomeric condensation product is etherified with one or more substituents to afford ether moieties randomly selected from the group consisting of vinylbenzyl, alkyl moieties containing from 1 to 10 carbon atoms, cycloalkyl moieties from 5 to 10 carbon atoms, and benzyl, with the ratio of vinylbenzyl to other moieties being from 1:1 to about 6:1.

25      DESCRIPTION OF THE PREFERRED EMBODIMENTS  
Polymeric Resins

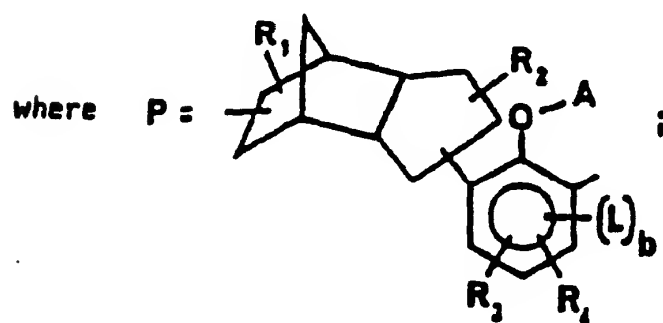
In U.S. Patent No. 4,824,920, one of the present inventors disclosed the preparation and use of ethers of the reaction product of a dicyclopentadiene with a phenol and their use in composites, especially laminated boards for electronic uses. It has now found that these compositions can be used as interlevel dielectrics, in combination with the oligomers of U.S. Pat. No. 4,816,498 where they have the advantages of low water absorption, low dielectric constant, low coefficient of thermal expansion, high glass transition

temperatur , high thermal stability, high solids coating concentrations, photochemical curability, thermal curability, and little or no volatiles generated during the cure process.

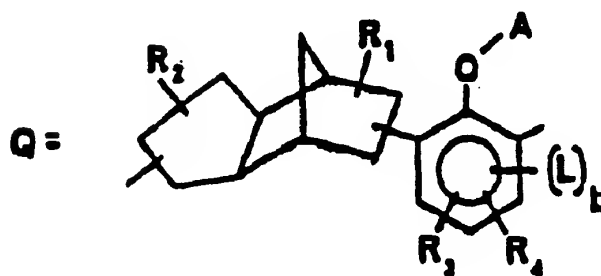
5 The prepolymers used in forming a pattern have the formula



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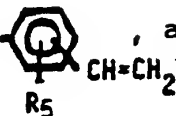
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with  $R_1, R_2 = H$  or alkyl of 1-10 carbon atoms;

$R_3 = \text{methyl}$ ;

$R_4 = H$ ;

$A = H, -CH_2$  , an alkyl moiety containing 1

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to 10 carbon atoms, a cycloalkyl moiety having 5 to 10 carbon atoms, or benzyl, subject to the constraint that at least 50% of all A's are the vinyl benzyl moiety;

10  $L = Br$  or  $Cl$ ;

$a = 0, 1, \text{ or } 2$ ;

$b = 0$  or  $1$ ;

$m, n, s, \text{ and } t$  are 0 or an integer, and  $m+n+s+t=z$  is an integer from 1-10; and

15  $R_5 = H, \text{ an alkyl moiety of 1-10 carbon atoms, a halogen or alkoxy moiety, or a monovalent aromatic radical.}$

The dicyclopentadiene portion can be substituted in either ring.  $R_1$  and  $R_2$  usually are  
20 hydrogen, that is, an unsubstituted dicyclopentadiene is preferred in the practice of this invention but each of  $R_1$  and  $R_2$  can be an alkyl group, preferably a primary alkyl group, containing up to about 10 carbon atoms. The lower alkyl groups, such as methyl, ethyl, propyl,  
25 and butyl, are especially preferred where the dicyclopentadiene is substituted. Substitution can be at any position of the dicyclopentadiene ring system but it is preferred that  $R_1$  be at a carbon of the 5-member ring not bonded to the aryl group, and that  $R_2$  is  
30 at the bridge or bridgehead carbon of the bicyclic ring portion.

The phenolic termini of our resins as well as the phenolic portion of P or Q may be substituted by a methyl group or a halogen atom. For the condensation  
35 with dicyclopentadiene mixtures of such phenols also may be used. The methyl group is at a position meta

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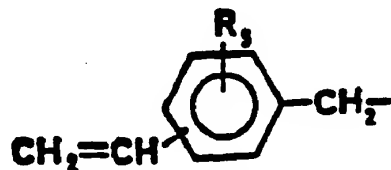
or para to the position bearing the oxygen atom. A para-substituted phenol is preferred in the practice of this invention because such a mixture tends to afford an amorphous resin, which is a beneficial feature, and is susceptible to photochemical curing.

The basic resins also can be readily modified to be flame retardant by incorporating halogen atoms into the aromatic rings. Thus, L may be a halogen atom, especially bromine, and where the aromatic ring is halogenated a is 0, 1 or 2 and b is 0 or 1. Polyhalogenated materials are desired as flame retardants, which means that a and b are recommended to be maximized. Where the aromatic rings are not halogen substituted then both a and b are 0.

The fragments P and Q are subunits of the adduct. Where the adduct is an oligomer it may be a head-to-head, head-to-tail, or completely or partially random arrangement. Where oligomers are formed they are of relatively low molecular weight. The variables m, n, s, and t each are integers such that z, where z equals  $m + n + s + t$ , is an integer from 1 to 10, and usually is up to about 5, with z being 3 or 4 preferred in the practice of our invention.

The phenolic hydroxyls in the adduct are capped so as to be converted to ethers. At least 80% of the phenolic groups are so capped, and it is desirable that at least 90%, and even more desirable that at least 95%, of the phenolic groups be capped. Stated differently, in the formula above less than about 20% of the A moieties are hydrogen, and desirably less than 10%, even more desirably less than 5%, are hydrogen.

The best case results where the ether portion, A, is a vinylbenzyl moiety, that is, of the structure



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where the vinyl group is either meta or para to the CH<sub>2</sub>, where R<sub>5</sub> is hydrogen, and which usually is a mixture of the meta- and para-isomers. R<sub>5</sub> is a chemically inert substituent selected from the group consisting of hydrogen, alkyl moieties containing from 1 to about 10 carbon atoms, the halogens, alkoxy moieties containing from 1 to about 10 carbon atoms, and monovalent radicals whose parent is an aromatic hydrocarbon.

However desirable it may be to have all the phenolic hydroxyls end-capped with vinylbenzyl moieties, there is a decided cost advantage when fewer than all of the other groups are vinylbenzyl usually at the expense of a somewhat lower dielectric constant. In our invention it is required that at least 50% of the A moieties different from hydrogen be a vinylbenzyl moiety, but a product with better performance characteristics results when from 70 to 100% of the ether groups are vinylbenzyl, and the best product results when 95 to 100% of such groups are vinylbenzyl. In many applications less than complete end-capping with vinyl benzyl groups is acceptable, but all of the hydroxyl groups should be capped.

In those cases where less than all of the ether groups are vinylbenzyl, then we are partial to resins where A is an alkyl group containing from 1 to 10 carbons, a cycloalkyl group having 5 to 10 carbons, or a benzyl group. Where A is an alkyl group, the primary alkyl groups are given priority, especially the primary lower alkyl groups containing from 1 to 4 carbon atoms. Thus, the most desirable alkyl groups consist of methyl, ethyl, 1-propyl, 1-butyl, and 2-methyl-1-propyl. Other alkyl groups are represented by 1-pentyl, 1-hexyl, 1-heptyl, 1-octyl, 1-nonyl, 1-decyl, 2-methyl-1-butyl, 3-methyl-1-butyl, 2,3-dimethyl-1-butyl, 3,3-dimethyl-1-butyl, 2-methyl-1-pentyl, and so forth. However, it is to be emphasized that a benzyl

group also operates quite satisfactorily in the practice of our invention. The most common cycloalkyl groups used in our invention are 5- and 6-membered cycloalkanes, unsubstituted or alkyl substituted so as to contain 5 to 10 carbon atoms. Examples are cyclopentyl, cyclohexyl, methylcyclopentyl, dimethylcyclopentyl, ethylcyclopentyl, propylcyclopentyl, butylcyclopentyl, pentylcyclopentyl, ethylmethylcyclopentyl, methylpropylcyclopentyl, butylmethylcyclopentyl, methylcyclohexyl, dimethylcyclohexyl, ethylcyclohexyl, propylcyclohexyl, butylcyclohexyl, and so forth. The 1-propyl group is an especially desirable alternative to the vinylbenzyl moiety, and resins where less than 5% of the A groups are hydrogen with the remainder being vinylbenzyl or 1-propyl in a ratio from 1:1:1 to about 6:1 are highly recommended. In a preferred embodiment, A is at least 70% vinyl benzyl and the remaining A's are propyls.

The use of a mixture tends to promote formation of an amorphous resin which is desirable both in increasing the solubility of the resin in a solution, in promoting good film-forming qualities, and in providing a stable, non-flaking coating. A desirable mixture of resins is one which consists of from about 5 to about 20% by weight of a resin where  $z = 1$ , about 10 to about 30% with  $z = 2$ , about 5 to about 30% with  $z = 3$ , about 5 to about 30% with  $z = 4$ , and about 5 to about 30% with  $z = 5-10$ .

The appended vinyl groups are readily crosslinked in a curing step effected by thermal, chemical, or radiative means. Thermal curing is generally done in the temperature range between about 100 and about 300°C, and in practice at a temperature between about 150 and about 200°C for 0.5-5 hours with post curing at about 180-300°C for about 0.5 -24 hours. Curing also may be brought about using a free radical

initiator, such as azo-bis-isobutyronitrile, benzoyl peroxide, di-t-butyl peroxide, etc. Curing may be effected as well as irradiation, especially by visible and ultraviolet light in the presence of a suitable photoinitiator or sensitizer. Whether thermal, chemical, or photochemical curing is performed, the resin becomes extensively crosslinked and sets to an infusible, insoluble glassy solid.

The resins of this invention may be prepared by an convenient method known in the art. However, they are most readily prepared by reacting a vinylbenzyl halide with the dicyclopentadiene-phenol adduct in a basic solution. Generally a mixture of the meta- and para-isomers of vinylbenzyl chloride are used, although the bromide and, to a lesser extent, the iodide also may be used. The reaction may be conveniently performed in an alcoholic potassium hydroxide solution, often containing acetone, N-methylpyrrolidone, or some other organic cosolvent, at the reflux temperature. Where some of A are alkyl, cycloalkyl, or benzyl moieties these may be prepared by reacting a suitable alkyl, cycloalkyl, or benzyl halide with a partially vinylbenzyl end-capped adduct, or by reacting the uncapped adduct with a mixture of halides.

The second type of oligomers are ethers of oligomeric condensation products of 1 molar proportion of certain dialdehydes with from about 3 to about 4 molar proportions of a phenol. More particularly, the ether moiety is randomly selected from among the vinylbenzyl moiety, alkyl moieties containing from 1 to 10 carbon atoms, cycloalkyl moieties having from 5 to about 10 carbon atoms, and the benzyl moiety, where the ratio of the vinylbenzyl to other ether moieties is at least 1:1 and may be as great as 6:1.

The phenolic oligomers are the condensation products of 1 molar proportions of selected dialdehydes

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with 3 to 4 molar proportions of a phenol. Although more than 4 molar proportions of a phenol can be used in the practice of this invention, no more than 4 molar proportions will react with the dialdehydes.

5 One class of dialdehydes which may be used in this invention are the linear, terminal alkylene dialdehydes of formula  $\text{OHC}(\text{CH}_2)_r\text{CHO}$  where  $r$  is 0 or an integer from 1 to 6. Such dialdehydes include glyoxal, malondialdehyde, succinidialdehyde, glutaraldehyde, 10 adiphaldehyde, pimelaldehyde, and sebacaldehyde. Those aldehydes where  $n$  is 0-4 are particularly preferred, and glyoxal ( $n=0$ ) is especially favored in the practice of this invention.

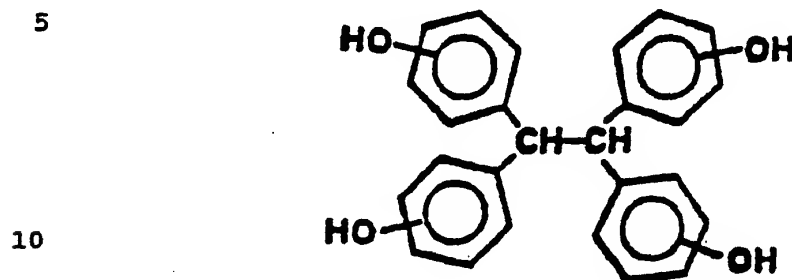
Other aldehydes which may be employed in 15 preparation of the oligomeric condensation products include cyclopentanedialdehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, the hexahydrophthalaldehydes (i.e., the reduced counterpart of the phthalaldehydes where the aromatic ring has been 20 reduced to a cyclohexane ring), cycloheptanedialdehyde, and cyclooctanedialdehyde.

The oligomers are the condensation product of 1 molar proportion of the aforementioned dialdehydes with from 3 to about 4 molar proportions of a phenol. 25 The phenol has the general structure  $\text{R}_6\text{C}_6\text{H}_4\text{OH}$  where  $\text{R}_6$  is hydrogen or an alkyl group containing from 1 through about 8 carbon atoms. The most desirable phenol is phenol itself, that is, the case where  $\text{R}_6$  is hydrogen. Where  $\text{R}_6$  is an alkyl group it is most desirable that the 30 alkyl group contain from 1 to about 4 carbon atoms, and cresol, the case where  $\text{R}_6$  is a methyl group is another preferred species of phenol.

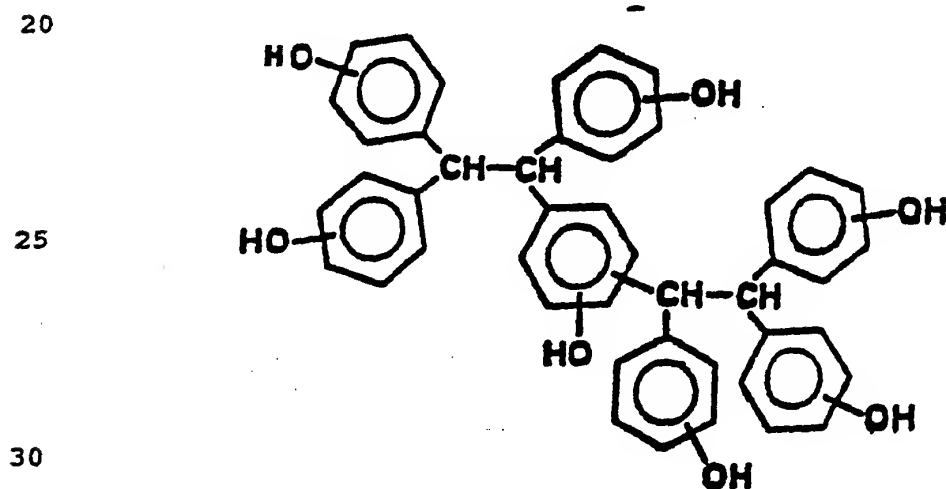
The condensation product is analogous to phenol-formaldehyde resins. That is, the products 35 result from the condensation of 2 molar proportions of a phenol with each aldehyde group. In the simplest

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case, which can be looked as the "monomeric" product, using phenol and glyoxal to exemplify the reaction, the product has the structure

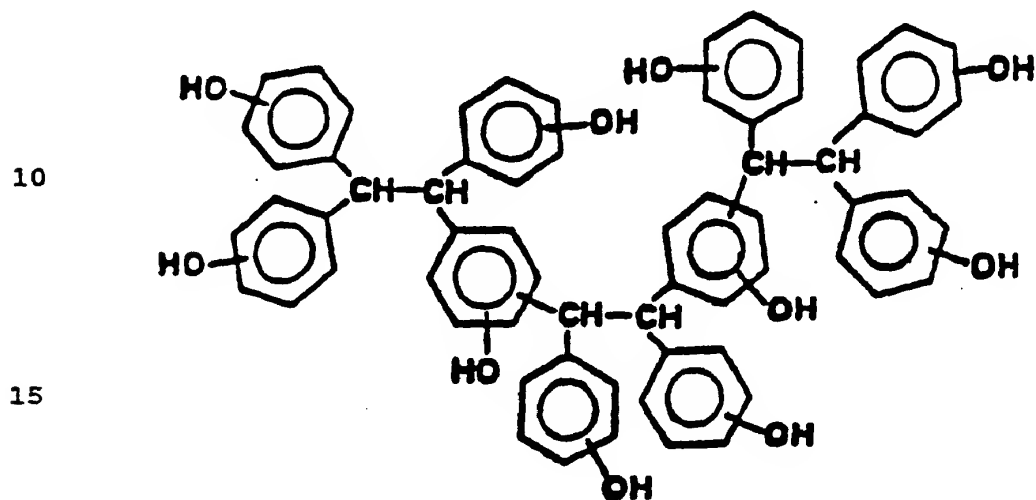


where the hydroxyls are almost exclusively ortho and para, and largely para, to the point of condensation of the phenol and glyoxal. However, the product above has 4 phenolic groups per molecule, and any one of these may react with another molecule of glyoxal which then further condenses with three other molecules of phenol to give the structure



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The oligomeric product above results from a molar proportion of 7 phenols to 2 glyoxals. This oligomer in turn can react with another molecule of glyoxal and the latter can react further with 3 additional phenols to give the next higher oligomer of the structure



which has the molar ratio of 10 phenolic groups to 3 glyoxals. In a similar fashion, the next higher oligomer has a molar ratio of phenol to glyoxal of 13:4, the next higher of 16:5, and so forth, with the limiting molar ratio being 3:1. It needs to be mentioned that a ratio less than 3:1 will never be achieved without internal cyclization, i.e., one molecule of glyoxal is required to react with at least 2 phenolic moieties of the oligomer. In a similar fashion, the condensation product which is the "monomer" has a limiting ratio of phenol-glyoxal of 4:1.

The condensation products are themselves phenols, as mentioned above, and are a mixture of oligomers. This mixture can be characterized by the number of phenolic moieties per molecule. We are concerned with those condensation products which have from 4 to about 60 phenolic moieties per molecule, and

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more usually between four and about 22 phenolic moieties per molecule. The product being a mixture of oligomers, the preferred mixture is characterized by having as an average between about 5 and about 8  
5 phenolic moieties per molecule.

More specifically, where the dialdehyde is glyoxal and the phenol is phenol itself each oligomeric product has a molecular weight between about 400 and 6000, and more desirably between about 400 and about  
10 2200. The mixture of oligomeric products may be characterized by an average molecular weight of between about 500 and about 800.

The interlevel dielectric resins of this invention are ethers of the aforescribed oligomeric  
15 condensation products. In one variant of our invention the phenolic condensation products are halogenated prior to ether formation in order to make the final resins more flame retardant. Increased flame retardancy occurs especially when the halogen is  
20 chlorine or bromine, and the use of a brominated product is preferred. The halogen is introduced into positions ortho and para to the phenolic hydroxyl group. If all of the ortho and para positions are available a maximum of three halogen atoms per phenolic  
25 moiety may be introduced. Often it is desirable to prepare the maximally halogenated oligomeric condensation product, although at times a halogen content less than the maximum is advantageous. However, in the latter variant it should be clear that  
30 there is at least one chlorine or bromine atom per phenolic moiety. The phenolic condensation products are capped so as to convert substantially all (greater than about 99.5%) of the hydroxyls to ether moieties. Each of the ether moieties is randomly selected from  
35 the group consisting of vinylbenzyl, alkyl containing 1 to 10 carbon atoms, cycloalkyl of from 5 to 10 carbon

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atoms, and benzyl moieties as described above with respect to the first type of oligomer where the ratio of the vinylbenzyl to all other ether moieties is at least 1:1 and may be as high as 6:1.

5           The prepolymers may be prepared by acid catalyzed condensation of phenols with dialdehydes followed by end-capping substantially all the phenolic hydroxyls by converting them to ethers. Acid catalyzed condensation is preferred to avoid the  
10 formation of terminal hydroxyl methylene groups,  $-\text{CH}_2\text{OH}$ . End-capping by ether formation can be effected by any suitable means, such as by reacting the phenolic condensation product with an alkyl or benzyl halide in a basic medium.

15           The resulting interlevel dielectric oligomers may be polymerized with attendant crosslinking by a variety of curing means. When curing is effected by thermal means, it generally is autoinitiated by heating the oligomer resin in air at a temperature between  
20 about 100 and 300°C., and more particularly between about 120 and 200°C. Curing also may be brought about by chemical means using a free radical initiator such as azo-bis-isobutyronitrile, benzoyl peroxide, di-*t*-butyl peroxide, etc. In the present invention curing  
25 is begun by irradiation, especially by visible and ultraviolet light in the presence or absence of a suitable photoinitiator or sensitizer, followed by thermal curing to produce an infusible, insoluble glassy solid.

30

#### Photodefinable Applications

          The oligomers may be used as a passivant, as an interlevel dielectric, as a means of providing device deep dielectric isolation (insulator isolating  
35 tranches), as a high temperature solder mask, a photoresist, etc. Although much of what follows

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describes its use primarily as an interlevel dielectric, the skilled worker will recognize from this description how to use the materials of this invention in other applications as well.

5           The oligomers are applied as a coating to a suitable substrate. For the most part the substrates used will be a silicon wafer, a silicon chip of an integrated circuit, a printed circuit board or a ceramic substrate. The photosensitive oligomers may be  
10 applied by spin coating, spray coating, by use of a doctor knife, or any other conventional techniques known in the art to obtain a uniform coating. Where the viscosity is too high, a solution of the resin in a suitable solvent may be used. The oligomers are  
15 soluble in a broad class of solvents including polar aprotic solvents, aromatic hydrocarbons, halogenated hydrocarbons, ketones, ester, and so forth. Examples of solvent which may be employed in the practice of our invention include dimethylformamide (DMF),  
20 hexamethylphosphoramide (HMPA), N-methylacetamide (NMAc), dimethylsulfoxide (DMSO), N-methylpyrrolidone (NMP), benzene, toluene, xylene, dichloromethane, chloroform, carbon tetrachloride, chlorobenzene, tetrachloroethane, tetrachloroethylene,  
25 trichloroethane, gamma-butyrolactone, methyl ethyl ketone, diethyl ketone, hexanone, heptanone, octanone, methyl acetate, ethyl acetate, methoxy ethanol, ethoxy ethanol, and so forth. The solvent should be unreactive with both the substrate and the  
30 photosensitive oligomers and able to dissolve the resins to provide at least about a 10 weight-volume percent solution. Since the solvent is typically removed prior to further processing, it is also preferable that as low boiling a solvent as possible be  
35 used consistent with the foregoing considerations.

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Although the oligomers may be photopolymerized directly, a photosensitizer or photoinitiator may be used and may be useful to decrease irradiation time. Where a photosensitizer or photoinitiator is used it will be added with the oligomers at the coating stage and will be present in an amount from about 0.001 to about 5.0 weight percent relative to the oligomers. Examples of photosensitizers or photoinitiators which may be successively used in the practice of this invention include such materials as benzophenone, 4,4'-bis(dimethylamino)benzophenone, xanthone, acetophenone, 4-trifluoromethyl-acetophenone, triphenylene, thioxanthone, anthraquinone, 4-phenylbenzophenone, naphthalene, 2-acetonaphthalene, 1-acetonaphthalene, chrysene, anthracene, 9,10-dichloroanthracene, pyrene, triphenylene, 1-fluoronaphthalene, 1-chloronaphthalene, 1-bromonaphthalene, 1-iodonaphthalene, 1,3-dicyanobenzene, dimethyl isophthalate, diethyl isophthalate, methyl 3-cyano-benzoate, ethyl 3-cyano-benzoate, phenyl 3-cyano-benzoate, 2,2-dimethoxyacetophenone, 2,2-diethoxyacetophenone, 2,2'-dimethoxy-2-phenylacetophenone, 2,2'-diethoxy-2-phenylacetophenone, benzoin methyl ether, and 1-phenyl-1,2-propanedione-2-O-benzoyloxime. Preferred sensitizers include benzophenone, 4,4'-bis(dimethylamino)benzophenone, 1,3-dicyanobenzene, dimethyl isophthalate, diethyl isophthalate, methyl 3-cyano-benzoate, and phenyl 3-cyano-benzoate.

Where the photosensitive oligomers have been applied as a solution to the substrate the solvent used must be removed prior to irradiation. Consequently, it is conventional to heat the coated substrate for a time sufficient to remove essentially all of the solvent present, if any, prior to irradiation, a stage known as the "softbake." It is for this reason that the use of

a low boiling solvent is preferred. It is acceptable to use enough heat to provide a semicured coating, especially since the oligomers may begin to cure at temperatures as low as about 110°C. The softbake can  
5 be carried out in vacuum, under an inert atmosphere (e.g., nitrogen, helium, argon, etc.) or in air.

A mask containing the desired pattern or image is placed on or adjacent to the coated substrate and the oligomeric coating is then irradiated through  
10 the mask by x-ray, electron beam, ion beam, ultraviolet, or visible radiation. For reasons of economy and ease of fabrication it is preferred to use radiation in the range from about 200 to about 800 nanometers. Since lower wave length radiation tends to  
15 afford better resolution, irradiation in the 200-500 nm range is preferred. With this treatment the irradiated portion of the coating becomes crosslinked so that the photocrosslinked oligomer is rather insoluble in the same solvent in which the original photosensitive  
20 oligomers remain quite soluble.

Irradiation may be done in either the presence or absence of oxygen. Exposure time necessary for adequate photocrosslinking to afford the differential solubility characteristic sought depends  
25 upon the wavelength of the light used, its intensity, the presence or absence of a photosensitizer or photoinitiator, and so forth, with a variation from a few seconds up through several minutes. For production purposes the shorter exposure times are highly  
30 preferred. One desirable characteristic of the photosensitive oligomers of this invention is that they photochemically crosslink throughout the thickness of the film, and therefore the pattern shows minimal undercutting upon development.

35 The selective pattern appears upon development with the solvent. As mentioned above, upon

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irradiation the photosensitive oligomeric resin becomes extensively crosslinked with a subsequent large differential solubility between the crosslinked, or irradiated, and non-crosslinked, or non-irradiated, portions of the oligomers. The solvents used in the development are in general the same ones used in preparing a solution of the oligomers for coating purposes. Thus, classes of solvents include aprotic solvents, aromatic hydrocarbons, halogenated hydrocarbons, ketones, esters, the Carbitols, and mixtures thereof.

Upon development selective patterns appear where the elevated portions correspond to the photochemically crosslinked oligomers. These relief structures are then thermally cured to afford a highly crosslinked, infusible, glassy solid highly resistant to elevated temperatures, chemical degradation, ion transport, and which serves as an effective protective layer and dielectric insulator. Curing is attended by crosslinking of the vinyl groups and may be effected either thermally, chemically, or photochemically, with thermal curing preferred. Thermal curing is generally done in the temperature range between about 100°C and about 300°C, and often is done in stages. So, for example, curing may first be effected at a temperature between about 150°C and about 200°C for 0.5-5 hours with postcuring at about 180°C-300°C for about 0.5-24 hours. Curing also may be brought about using a free radical initiator, such as azo-bis-isobutyronitrile, benzoyl peroxide, di-t-butylperoxide, and so on.

The oligomers of the invention have been found particularly useful in photodefinable applications since they may be coated as solutions with high solids levels and thus less solvent must be evaporated. Also, since no volatile by-products are

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generated during curing the shrinkage of the films is minimized.

#### MULTILAYER PROCESSING

5           The substrate (i.e., ceramic, alumina, silicon, printed wiring board, etc.) may be cleaned with conventional cleaning solvents (e.g., methylene chloride, chloroform, Genesolv®, trichloroethylene, ethanol, methanol, sodium bisulfite, sodium sulfite, 10 potassium sulfite, etc.) employing normal cleaning processes as known in the art. In addition, the substrate may contain circuitry already deposited upon it. The substrate may be utilized after the cleaning process or may be surface treated to promote adhesion 15 between the substrate and the metals and/or polymer dielectric layer.

          If used, an adhesion promoter between the substrate and the dielectric layer may be chosen from a range of surface silylating agents containing 20 reactive groups capable of reacting with the polymers of the invention. Examples of surface silylating agents which can be employed are: vinylmethyldimethoxysilane, vinyltrimethoxysilane, vinylmethyldiethoxysilane, vinyltriethoxysilane, 25 diethoxymethylvinylphenethylsilane, dimethoxymethylvinylphenethylsilane, triethoxyvinylphenethylsilane, trimethoxyvinylphenethylsilane, etc. Preferred silylating agents are vinylmethyldimethoxysilane, 30 vinylmethyldiethoxysilane, diethoxymethylvinylphenethylsilane, and dimethoxymethylvinylphenethylsilane. The surface silylating agent would be applied to the substrate via dipping, spin coating, or other techniques from an 35 alcohol-water solution. For example, a 1 to 10 wt.% solution of the silylating agent is dissolved in 85 to

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98 wt.% of alcohol (e.g., methanol, ethanol, isopropanol, etc.) and 1 to 13 wt.% of water. The substrate is dipped in this solution for 15 seconds to 5 minutes, air dried for 1 minute to 5 hours, and then  
5 soft baked for 1 minute to 5 hours at 60 to 100°C either in a convection oven, vacuum oven or hot plate.

The cleaned and/or surface treated substrate will be covered with a metal pattern before being covered with the dielectric layer of the invention.  
10 For example, a 500 to 1000 Å layer of chromium, 8000 to 20000 Å layer of copper and a 500 to 1000 Å layer of chromium may be sputtered onto the surface. Then, the metal layer is coated with a commercial photoresist and processed according to the recommended processing  
15 scheme utilizing a spin coat, soft bake, imaging, developing, and hard bake cycle. This exposes portions of the metal layer to be removed by etching to create the pattern. The metals are etched utilizing standard wet techniques, for example: The top chromium layer is  
20 etched with a 1 to 30 % hydrochloric acid solution activated with aluminum for 10 seconds to 5 minutes; the copper layer is etched with a sodium persulfate solution for 10 seconds to 10 minutes; the bottom chromium layer is etched with a 1 to 30 % hydrochloric  
25 acid solution activated with aluminum for 10 seconds to 5 minutes; and finally the etched substrate is washed with deionized water for 10 to 60 seconds. Then the remaining photoresist is stripped from the metal pattern as per the processing technique recommended for  
30 the photoresist. Finally the cleaned substrate is dried prior to the next processing step.

The dielectric layer is coated onto the substrate and its metal pattern and processed as follows: The prepolymer (e.g., 10 to 80 wt. %) solution in an appropriate solvent (toluene, NMP, DMF,  
35 etc.) is spin coated onto the substrate at a speed of

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500 to 2500 rpm for 30 to 90 seconds; the prepolymer coated substrate is soft baked at a temperature of 25 to 60°C for 15 minutes to 24 hours in a vacuum oven with or without a nitrogen bleed; the soft-baked coating is then imaged with a UV light source (220-320 nm range) for 15 seconds to 30 minutes employing a mask of desired design for vias and the like; the photocured polymer is then developed with an appropriate solvent system (e.g., toluene, toluene/hexane, toluene/ethanol, cyclohexane, etc.) at 25 to 35°C with or without ultrasonics or via spraying for 15 to 120 seconds; the developed substrate can then be exposed to a stop or rinse bath or solvent spray based upon a solvent system miscible with the developing solvent but a poor solvent for the polymer system (for example hexane, pentane, ethanol, etc.) (optional step); the vias are then cleaned with a plasma or wet etch; and finally the dried substrate is hard baked in vacuum or under an inert atmosphere (nitrogen, argon, etc.) with a cure cycle including a ramp from 25° to 300°C for 30 minutes to 2 hours, a hold at 300°C for 1 hour and then a cool down from 300° to 25°C with a 30 minute to 3 hour ramp.

The process is repeated as required in order to form an electronic interconnect structure of desired electrical and dielectric levels.

#### Example 1

##### Synthesis of Styrene Terminated Para-Cresol

##### Dicyclopentadiene (STPCDP (70VBz/30Pr))

200.0 grams of the para-cresol dicyclopentadiene (PCDP) from Borden Chemical (Mn = 520, Mw = 1100, dispersity of 2.12) was dissolved in 700 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction mixture was added 123.06 g (0.806 moles) of



vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.30 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 52.78 g (0.941 moles) of potassium hydroxide in 125 mL of methanol was added dropwise over a 30 minute interval. The reaction was maintained at 60°C for 16 hrs with stirring under a nitrogen purge. To this reaction mixture was added 31.32 g (0.254 moles) of n-propylbromide and then 15.34 g (0.273 moles) of potassium hydroxide in 80 mL of methanol over a 1 hr. interval. The reaction was maintained at 60°C for 3.5 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 2.0 Liters of toluene added and then washed thrice with 1.0 Liters of water, dried over magnesium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 630, Mw = 1200, dispersity of 1.9.

#### Example 2

##### Synthesis of Styrene Terminated Para-Cresol

Dicyclopentadiene (STPCDP (70VBz/30Pr))  
500.0 grams of the para-cresol dicyclopentadiene (PCDP) from Borden Chemical (Mn = 520, Mw = 1100, dispersity of 2.12) was dissolved in 1750 mL of N-methylpyrrolidinone (NMP) in a 5000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction mixture was added 307.65 g (2.016 moles) of vinylbenzylchloride (60/40 para/meta isomer ratio) and 1.43 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 131.95 g (2.35 moles) of potassium hydroxide in 312 mL of methanol was added dropwise over a 6.0 hrs. interval. The reaction was maintained at 60°C for 16 hrs. with stirring under a nitrogen purge. To this reaction mixture was added 78.30 g (0.637 mol s) of n-propylbromide, and then

added 38.35 g (0.630 moles) of potassium hydroxide in 200 mL of methanol over a 20 minute interval. The reaction was maintained at 60°C for 3.5 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 2.0 Liters of toluene added and then washed with 2.0 Liters of water, once with saturated sodium chloride solution, and finally washed with a saturated ammonium chloride solution, dried over magnesium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 500, Mw = 960, dispersity 1.9.

### Example 3

#### Synthesis of Styrene Terminated Para-Cresol

##### Dicyclopentadiene (STPCDP (70VBz/30Pr))

324.0 grams (2.996 moles) of para-cresol was charged into a 1000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, Therm-O-Watch, and Nitrogen purge. The reaction flask is heated to 90°C under nitrogen with stirring. To the melted p-cresol is added 6.0 mL (0.041 moles) of boron trifluoride etherate. To this reaction mixture was added 262.0 g (1.982 moles) of dicyclopentadiene over a 2.2 hour interval, the reaction was maintained at 90°C for 1 hour with stirring; then the unreacted p-cresol was vacuum distilled from the reaction mixture. The para-cresol dicyclopentadiene (PCDP) resin was isolated by pouring into a stainless steel pan and allowing to cool to ambient temperature; Mn = 650, Mw = 1500, dispersity of 2.31.

207.2 grams of the para-cresol dicyclopentadiene (PCDP) from above was dissolved in 700 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer,

nitrogen purge and Therm-O-Watch. To this reaction mixture was added 127.5 g (0.835 moles) of vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.20 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 54.68 g (0.975 moles) of potassium hydroxide in 130 mL of methanol was added dropwise over a 2.0 hours interval. The reaction was maintained at 60°C for 16 hrs with stirring under a nitrogen purge. To this reaction mixture was added 32.45 g (0.263 moles) of n-propylbromide, and then added 15.89 g (0.283 moles) of potassium hydroxide in 80 mL of methanol over an 1.33 hour interval. The reaction was maintained at 60°C for 8 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 1.5 Liters of toluene added and then washed thrice with 2.0 Liters of water, dried over magnesium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 770, Mw = 1400, dispersity of 1.82.

#### Example 4

#### Synthesis of Styrene Terminated Para-Cresol Dicyclopentadiene (STPCDP (70VBz/30Pr))

300.0 grams of para-cresol dicyclopentadiene (PCDP) from Borden Chemical (Mn = 520, Mw = 1100, dispersity of 2.12) and 420 mL of ortho-dichlorobenzene was charged into a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, Therm-O-Watch, and Nitrogen purge. The reaction mixture was heated to 60°C under nitrogen with stirring; after complete dissolution of PCDP then 6.0 mL (0.041 moles) of boron trifluoride etherate was added. To this reaction mixture was added 71.12 g (0.538 moles) of dicyclopentadiene over a 1.1 hour interval, the reaction was maintained at 60°C with stirring during the addition; then the reaction was

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h ated to 150°C for 4 hours. The ortho-dichlorobenzene and unreacted dicyclopentadiene was vacuum distilled from the reaction mixture. The para-cresol dicyclopentadiene (PCDP) resin was isolated by pouring  
5 into a stainless steel pan and allowing to cool to ambient temperature, yield 332.0 g; Mn = 800, Mw = 2500, dispersity of 3.12.

318.5 grams of the para-cresol dicyclopentadiene (PCDP) from above was dissolved in  
10 1100 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction mixture was added 195.0 g (1.278 moles) of  
15 vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.30 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 84.05 g (1.498 moles) of potassium hydroxide in 200 mL of methanol was added dropwise over a 3 hour interval. The reaction  
20 was maintained at 60°C for 16 hrs with stirring under a nitrogen purge. To this reaction mixture was added 49.88 g (0.406 moles) of n-propylbromide, and then 24.43 g (0.435 moles) of potassium hydroxide in 125 mL of methanol added over a 2 hour interval. The reaction  
25 was maintained at 60°C for 4 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 1.5 Liters of toluene added and then washed once with 4 Liters of water and twice with saturated sodium chloride  
30 solution, dried over magnesium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 700, Mw = 1600, dispersity of 2.3.

Example 5Synthesis of Styrene Terminated Para-Cresol  
Dicyclopentadiene (STPCDP (70VBz/30Pr))

324.0 grams (2.996 moles) of para-cresol was  
5 charged into a 1000 mL 4-neck resin kettle equipped  
with mechanical stirrer, addition funnel, condenser,  
thermometer, Therm-O-Watch, and Nitrogen purge. The  
reaction flask is heated to 90°C under nitrogen with  
stirring. To the melted p-cresol is added 6.0 mL  
10 (0.041 moles) of boron trifluoride etherate. To this  
reaction mixture was added 288.2 g (2.180 moles) of  
dicyclopentadiene over a 1.5 hour interval, the  
reaction was maintained at 90°C for 1 hour with  
stirring; then the unreacted p-cresol was vacuum  
15 distilled from the reaction mixture. The para-cresol  
dicyclopentadiene (PCDP) resin was isolated by pouring  
into a stainless steel pan and allowing to cool to  
ambient temperature, yield 456.0 g; Mn = 720, Mw =  
1900, dispersity of 2.64.

20 436.0 grams of the para-cresol  
dicyclopentadiene (PCDP) from above was dissolved in  
1200 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-  
neck round bottom flask equipped with mechanical  
stirrer, addition funnel, condenser, thermometer,  
25 nitrogen purge and Therm-O-Watch. To this reaction  
mixture was added 269.0 g (1.763 moles) of  
vinylbenzylchloride (60/40 para/meta isomer ratio) and  
0.45 g of 2,6-di-tert-butyl-p-cresol (BHT). The  
reaction mixture was heated to 60°C and 106.0 g (1.890  
30 moles) of potassium hydroxide in 250 mL of methanol was  
added dropwise over a 2.5 hour interval. The reaction  
was maintained at 60°C for 16 hrs with stirring under  
a nitrogen purge. To this reaction mixture was added  
102.0 g (0.829 moles) of n-propylbromide was added to  
35 the reaction mixture and heated with stirring under  
purge to 60°C. To this reaction mixture was then added

35.4 g (0.631 moles) of potassium hydroxide in 120 mL of methanol over a 1.5 hour interval. The reaction was maintained at 60°C for 3 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 4 Liters of toluene added and then washed four times with 2.0 Liters of water and once with saturated sodium chloride solution, dried over sodium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 780, Mw = 1600, dispersity of 2.1.

#### Example 6

#### Synthesis of Styrene Terminated Para-Cresol Dicyclopentadiene (STPCDP (70VBz/30Pr))

628.0 grams (5.807 moles) of para-cresol was charged into a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, Therm-O-Watch, and Nitrogen purge. The reaction flask is heated to 90°C under nitrogen with stirring. To the melted p-cresol is added 12.0 mL (0.082 moles) of boron trifluoride etherate. To this reaction mixture was added 524.0 g (3.963 moles) of dicyclopentadiene over a 3.0 hour interval, the reaction was maintained at 90°C for 1 hour with stirring; then the unreacted p-cresol was vacuum distilled from the reaction mixture. The para-cresol dicyclopentadiene (PCDP) resin was isolated by pouring into a stainless steel pan and allowing to cool to ambient temperature, yielding 612.2 g of resin; Mn = 990, Mw = 2900, dispersity of 2.93.

591.2 grams of the para-cresol dicyclopentadiene (PCDP) from above was dissolved in 2100 mL of N-methylpyrrolidinone (NMP) in a 5000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction mixture was added 364.6 g (2.389 mol s) of

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vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.6 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 147.4 g (2.627 moles) of potassium hydroxide in 325 mL of methanol was added dropwise over a 2 hour interval. The reaction was maintained at 60°C for 6 hrs with stirring under a nitrogen purge. To this reaction mixture was added 157.0 g (1.276 moles) of n-propylbromide, and then 71.82 g (1.280 moles) of potassium hydroxide in 165 mL of methanol was added over a 2 hour interval. The reaction was maintained at 60°C for 4 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 4.0 Liters of toluene added and then washed thrice with 2.0 Liters of water, dried over sodium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 740, Mw = 1500, dispersity of 2.03.

#### Example 7

#### 20      Synthesis of Styrene Terminated Para-Cresol          Dicyclopentadiene (STPCDP (70VBz/30Pr))

500.0 grams of para-cresol dicyclopentadiene (PCDP) from Borden Chemical (Mn = 520, Mw = 1100, dispersity of 2.12) and 500 mL of ortho-dichlorobenzene was charged into a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, Therm-O-Watch, and Nitrogen purge. The reaction mixture was heated to 60°C under nitrogen with stirring; after complete dissolution of PCDP then 1.0 mL ( $6.83 \times 10^{-3}$  moles) of boron trifluoride etherate was added. To this reaction mixture was added 71.12 g (0.538 moles) of dicyclopentadiene over a 45 minute interval, the reaction was maintained at 60°C with stirring during the addition; then the reaction was heated to 150°C for 4 hours, and then cooled to ambient temperature. The

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reaction mixture was coagulated by addition to methanol, filtered, and then dried in a vacuum oven at 80°C overnight; Mn = 700, Mw = 1500, dispersity of 2.14.

5           308.0 grams of the para-cresol dicyclopentadiene (PCDP) from above was dissolved in 1050 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction  
10 mixture was added 189.0 g (1.238 moles) of vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.20 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 76.82 g (1.370  
15 moles) of potassium hydroxide in 225 mL of methanol was added dropwise over a 1.75 hour interval. The reaction was maintained at 60°C for 4.2 hrs with stirring under a nitrogen purge. To this reaction mixture was added  
20 78.83 g (0.640 moles) of n-propylbromide, and then 35.91 g (0.640 moles) of potassium hydroxide in 125 mL of methanol added over a 2.0 hour interval. The reaction was maintained at 60°C for 16 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel,  
25 and 3 Liters of toluene added and then washed thrice with 2.0 Liters of water, dried over magnesium sulfate, filtered and concentrated under vacuum, yielding 332.0 g of red resinous product; Mn = 670, Mw = 1300, dispersity of 1.9.

#### Example 8

30

#### Synthesis of Styrene Terminated Para-Cresol Dicyclopentadiene (STPCDP (65VBz/35Pr))

500.0 grams of para-cresol dicyclopentadiene (PCDP) from Borden Chemical (Mn = 520, Mw = 1100, dispersity of 2.12) and 500 mL of ortho-dichlorobenzene  
35 was charged into a 2000 mL 3-neck round bottom flask



equipped with mechanical stirrer, addition funnel, condenser, thermometer, Therm-O-Watch, and Nitrogen purge. The reaction mixture was heated to 60°C under nitrogen with stirring; after complete dissolution of PCDP then 1.0 mL ( $6.83 \times 10^{-3}$  moles) of boron trifluoride etherate was added. To this reaction mixture was added 59.26 g (0.448 moles) of dicyclopentadiene over a 2 hour interval, the reaction was maintained at 60°C with stirring during the addition; then the reaction was heated to 150°C for 4 hours, and then cooled to ambient temperature. The reaction mixture was coagulated by addition to methanol, filtered, and then dried in a vacuum oven at 80°C overnight; Mn = 630, Mw = 1400, dispersity of 2.22.

146.22 grams of the para-cresol dicyclopentadiene (PCDP) from above was dissolved in 600 mL of N-methylpyrrolidinone (NMP) in a 2000 mL 3-neck round bottom flask equipped with mechanical stirrer, addition funnel, condenser, thermometer, nitrogen purge and Therm-O-Watch. To this reaction mixture was added 64.76 g (0.424 moles) of vinylbenzylchloride (60/40 para/meta isomer ratio) and 0.15 g of 2,6-di-tert-butyl-p-cresol (BHT). The reaction mixture was heated to 60°C and 23.81 g (0.424 moles) of potassium hydroxide in 60 mL of methanol was added dropwise over an 1.2 hour interval. The reaction was maintained at 60°C for 4.0 hrs with stirring under a nitrogen purge. To this reaction mixture was added 40.14 g (0.326 moles) of n-propylbromide, and then added 18.32 g (0.327 moles) of potassium hydroxide in 40 mL of methanol added over an 1 hour interval. The reaction was maintained at 60°C for 4 hours and then allowed to cool to room temperature. The reaction mixture was then transferred to a separatory funnel, and 1 Liter of toluene added and then washed thrice

with 1 Liter of water, dried over sodium sulfate, filtered and concentrated under vacuum, yielding a red resinous product; Mn = 710, Mw = 1400, dispersity of 1.97.

5

Example 9Synthesis of Styrene-Terminated Tetraphenol Ethane  
(70% Vinylbenzyl/30% Propyl)(STTPE(70 VBz/30 Pr))

To a 250 mL round bottom, 3-neck flask equipped with a stirring shaft, an addition funnel and  
10 a condenser was added 25.0 g tetraphenol ethane (TPE) (Mn=274, Mw=711) (0.0354 mol), 0.23 g BHT (0.00106 mol) and 120 mL N-methyl pyrrolidinone (NMP). Upon dissolution of the TPE, 26.48 g vinylbenzyl chloride (VBC) (0.174 mol) were added and the vessel flushed and  
15 placed under positive nitrogen pressure by means of a mineral oil bubbler. The solution was heated to 60°C by means of a water bath and 11.34 g KOH (0.177 mol) dissolved in 25 mL of methanol were added dropwise over 30 minutes. The mixture was kept at 60°C for an  
20 additional 3.5 hours, 9.0 mL 1-bromopropane (0.099 mol) were then added. 4.86 g KOH (0.0758 mol) dissolved in 11 mL methanol were then added dropwise over 30 minutes and the temperature maintained at 50°C an additional 1.5 hours.

25 The mixture was cooled and slowly added to 600 mL of methanol leaving a solid yellow mass. The methanol was decanted and the solids along with fresh methanol were placed in a blender to produce an oily solid which was collected on a Buchner funnel. This  
30 material was dissolved in dichloromethane and washed with 4 x 500 mL water. The organic phase was dried over sodium sulfate and filtered through Celite. Solvent was removed by rotary evaporation leaving an orange semi-solid, 49% yield. GPC examination of resin  
35 indicates Mn=1040, Mw=1290, dispersity 1.24. Infrared examination of resin indicates some residual OH (<5%),

ion chromatography indicates: 17 ppm Cl<sup>-</sup>, <1 ppm Br<sup>-</sup>,  
1 ppm SO<sub>4</sub><sup>-2</sup>.

#### Example 10

##### Synthesis of Styrene Terminated Tetraphenol Ethane

5                    (100% Vinylbenzyl)(STTPE (100 VBz))

To a 2-L, 3-neck round bottom flask equipped  
with a stirring shaft, an additional funnel and a  
condenser was added 200.0 g tetraphenol ethane (TPE)  
(Mn=274, Mw=711) (0.284 mol), 1.88 g BHT (0.00852 mol)  
10 and 950 mL N-methyl pyrrolidinone (NMP). Upon  
dissolution of the TPE 242.65 g vinylbenzyl chloride  
(VBC) (1.59 mol) were added and the vessel flushed and  
placed under positive nitrogen pressure by means of a  
mineral oil bubbler. The solution was heated to 60°C  
15 by a water bath and 101.95 g KOH (1.59 mol) dissolved  
in 230 mL of methanol were added dropwise over 30  
minutes. The mixture was kept at 60°C, for an  
additional 4.7 hours, 15.17 g VBC (0.0994 mol) were  
then added. 6.37 g KOH (0.0994 mol) dissolved in 15 mL  
20 methanol were then added dropwise. A final identical  
addition of VBC and KOH/methanol was made 1.7 hours  
later and the reaction maintained at 60°C for 1 hour  
longer.

The mixture was cooled and 1.2 L toluene were  
25 added. The mixture was washed with 1X3 L water and 2X3  
L 1M NaCl (aq). The organic phase was dried over  
sodium sulfate, slurried with Celite and filtered.  
Solvent was removed by rotary evaporation up to 40°C at  
3 torr leaving a viscous brown resin, 95% yield. GPC  
30 analysis found Mn=778, Mw=1079, dispersity 1.39;  
Infrared analysis indicates no residual hydroxyl  
(<0.5%); Ion Chromatography found: 45 ppm Cl<sup>-</sup>.

#### Example 11

A series of styrene terminated para-cresol  
35 dicyclopentadiene (STPCDP) of Examples 6, 7, 8, 4, and  
5 corresponding respectively to Samples 1, 2, 3, 4, and

5 were cured via the following cure cycle 2 hrs at 80°C, 16 hrs. at 100°C, 4 hrs. at 120°C, 16 hrs. at 160°C, 2 hrs. at 200°C and then 1 hr. at 225°C. Properties of the cured resins are given in the following table.

Table A  
STPCDP Properties

Sample No.	1	2	3	4	5
Tg (°C) <sup>(a)</sup>	>300	>300	>300	>300	>300
Tsp (°C) <sup>(b)</sup>	177±8	160±5	179±6	135±5	173±7
$\alpha_{sp}$ (ppm/°C) <sup>(c)</sup>	42±2	55±9	71±6	66±10	57±5
$\alpha_{260}$ (ppm/°C) <sup>(d)</sup>	96±7	85±12	155±4	125±5	86±2
$\epsilon'$ <sup>(e)</sup>	2.73	2.86	2.78	2.72	2.70
$\tan \delta$ <sup>(f)</sup>	0.0009	0.0001	0.001	0.0004	0.003
$\epsilon'$ <sup>(g)</sup>	2.75	2.89	2.80	2.74	2.74
$\tan \delta$ <sup>(h)</sup>	0.004	0.004	0.005	0.002	0.002
% Water <sup>(i)</sup> Absorption	0.145	0.156	0.161	0.089	0.107

(a) glass transition temperature by differential scanning calorimeter

(b) softening point by Thermo Mechanical Analysis - minor thermal transition

(c) coefficient of thermal expansion between 25°C and softening point

(d) coefficient of thermal expansion between 25° and 260°C

(e) dielectric constant at 1 MHz and 0% Relative Humidity at 25°C

(f) loss tangent at 1 MHz and 0% Relative Humidity at 25°C

(g) dielectric constant at 1 MHz and 50% Relative Humidity at 25°C

(h) loss tangent at 1 MHz and 50% Relative Humidity at 25°C

5 (i) at 50% Relative Humidity, 25°C for 168 hours

#### Example 12

A series of coating solutions were prepared and used to coat silicon surfaces. The solution concentration was 56 wt. % STPCDP from Example 6 in  
10 toluene. The solution was applied by spin coating at 950 rpm for 60 seconds. The coated discs were soft baked at 25°C for 18 hours under vacuum. Then, they were exposed for 3 minutes to UV irradiation with a 300 watt mercury vapor lamp with a quartz/water filter.  
15 The irradiated coatings were then exposed to various solvents and the amount of cured resin dissolved was measured. The results are shown in the following tables.

Table B

20

% STPCDP<sup>(a)</sup> Removed

Solvent (Toluene:Ethanol)<sup>(b)</sup>

Time(sec)

		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
	0	0	0	0	0	0	0
25	30	2.16	2.69	0.83	0.56	0.84	0.88
	60	4.32	2.69	2.20	0.83	2.23	0.88
	90	3.51	2.44	2.20	0.56	2.23	1.46
	120	3.51	3.18	1.65	1.67	0.84	1.75
	180	3.24	2.69	0.00	2.78	0.84	1.75
30	300	5.68	4.89	1.38	1.67	0.00	-0.29

a) STPCDP coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.

35 b) Weight % solutions.

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Table C  
% STPCDP<sup>(a)</sup> Removed  
Solvent (Toluene:n-Hexane)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
5	0	0	0	0	0	0	0
	30	2.16	-0.90	-1.50	-1.45	-1.63	-1.42
	60	4.32	0.00	0.00	-0.87	0.00	-0.28
	90	3.51	0.30	0.00	-1.16	0.00	-0.28
	120	3.51	0.60	0.60	0.29	0.27	-0.57
10	180	3.24	0.30	1.20	0.00	0.82	0.00
	300	5.68	1.80	-0.30	-0.29	0.82	-0.28

- 15 a) STPCDP coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.
- b) Weight % solutions.

20 Tables B and C may be compared with the results of Tables D and E below in which only the soft bake was carried out and no curing by UV radiation was done.

Table D  
% STPCDP<sup>(a)</sup> Removed  
Solvent (Toluene:Ethanol)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
25	0	0	0	0	0	0	0
	30	97.38	97.69	90.06	15.16	-4.02	0.00
	60	101.46	100.58	100.00	41.11	-0.93	0.00
	90	102.33	100.00	100.28	57.73	0.00	2.35
	120	102.04	100.00	99.72	63.56	1.55	1.76
30	180	101.46	100.29	100.57	69.68	2.79	-0.29
	300	100.00	100.29	100.57	74.34	0.93	-0.59

- 35 a) STPCDP coated on silicon wafer and soft baked at 25°C for 18 hrs.

b) Weight % solutions.

Table E

% STPCDP<sup>(a)</sup> Removed

Solvent (Toluene:n-Hexane)<sup>(b)</sup>

5	<u>Time(sec)</u>	<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
	0	0	0	0	0	0	0
	30	97.38	101.71	-2.82	-2.82	-3.42	-0.58
	60	101.46	103.43	12.43	87.32	9.97	-1.17
10	90	102.33	104.29	65.54	103.38	60.40	-0.58
	120	102.04	104.00	92.66	104.23	74.36	0.58
	180	101.46	104.00	96.33	102.82	83.19	-0.58
	300	100.00	104.29	100.56	102.82	85.75	-0.58

15 a) STPCDP coated on silicon wafer and soft baked at 25°C for 18 hrs.

b) Weight % solutions.

Example 13

A series of STPCDP solutions were prepared using various concentrations of STPCDP of Example 6 in toluene. These solutions were spin coated onto a silicon substrate (surface) utilizing spin coating rates from 600 rpm to 2000 rpm for 60 seconds; soft baked for 24 hours at 25°C under vacuum. The samples were then exposed for 3 minutes to UV irradiation with a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The air dried substrate was hard baked employing a cure cycle under vacuum of 25°C to 220°C ramp in 1 hour, held at 220°C for 2.5 hours and then cooled to room temperature.

The film thickness of the photocured polymer was analyzed employing a Taylor-Hobson Talysurf 10 profilometer. The following table illustrates the film thicknesses obtained.

Table F

5	STPCDP Solids Content <sup>a</sup>	Viscosity (mPa s)	Film Thickness ( $\mu$ m)					
			Spin Coating Speed (rpm)					
			600	700	800	1000	1500	2000
	36.7%	5.0	---	4.4	---	3.6	2.8	---
	50.0%	15.0	8.8	8.6	7.9	7.2	6.1	5.8
	52.6%	22.0	---	11.3	---	9.8	8.0	---
	55.6%	36.0	---	17.6	---	13.0	9.8	---

10

a) Dissolved solids content in Toluene

Example 14

A series of STPCDP solutions were prepared using various concentrations of STPCDP of Example 6 in  
 15 toluene. These solutions were spin coated onto a silicon substrate (surface) utilizing spin coating rates from 600 rpm to 2000 rpm for 60 seconds; soft baked for 24 hours at 25°C under vacuum. The samples were then exposed for 3 minutes to UV irradiation with  
 20 a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The air dried substrate was hard baked employing a cure cycle under vacuum of 25°C to 220°C ramp in 1 hour,  
 25 held at 220°C for 2.5 hours and then cooled to room temperature.

The film thickness and sidewall angle of the photocured polymer was analyzed utilizing a Sloan Technology Corporation Dektak 3030 profilometer. This  
 30 data is summarized in the following table.



Table G

	Spin Speed (rpm)	Film thickn ss	Sidewall Angle ( $\mu$ m)
5	600	10.0	31
	600	10.0	22
	600	11.5	13
	600	12.0	28
	700	10.8	16
10	700	8.5	9
	700	9.4	39
	700	11.3	39
15	800	9.7	13
	800	7.0	5
	800	9.0	11
	800	10.0	10
	1000	5.9	7
	1000	9.4	12
20	1000	8.5	22
	1000	8.3	17
25	1500	6.4	24
	1500	6.5	23
	1500	8.0	6
	1500	7.0	20
	2000	7.0	15
	2000	6.8	23
	2000	6.2	24
30			

Example 15

A series of STPCDP solutions were prepared using various concentrations of STPCDP of Example 6 in toluene. These solutions were spin coated onto a silicon substrate (surface) utilizing spin coating rates from 600 rpm to 2000 rpm for 60 s conds; soft baked for 24 hours at 25°C under vacuum. The samples

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were then exposed for 3 minutes to UV irradiation with a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The  
 5 air dried substrate was hard baked employing a cure cycle under vacuum of 25°C to 220°C ramp in 1 hour, held at 220°C for 2.5 hours and then cooled to room temperature. The samples were then metallized via ion-beam sputtering to yield a metal film of thickness 5000  
 10 to 10000 Å.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal shock cycling. A thermal shock cycle encompasses the following thermal cycling of the sample: hold at -55°C  
 15 for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes. In the following tables the ratio given means that of 25 squares of the metal, some to all of them were not removed by the tape. That is, 25/25 means that all the squares remained adhered to  
 20 the dielectric polymer while 5/25 means that 20 squares of metal were removed.

#### Adhesion Measurement Results

Metal Layer	Before Thermal Shock Cycling		After 92 Cycles		After 184 Cycles	
25	2.5	10.0	2.5	10.0	2.5	10.0
	1b. (b)	1b.	1b.	1b.	1b.	1b.
Chromium	8/25	8/8	8/8	8/8	7/8	6/7
	Passed	Passed	Passed	Passed	Passed	Passed
30 Chromium	0/25	-----	-----	-----	-----	-----
	Passed					
35 Copper	0/25	-----	-----	-----	-----	-----
	Passed					

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	Copper	0/25	-----	-----	-----	-----	-----
		Passed					
5	Aluminum	25/25	25/25	25/25	25/25	a	a
		Passed	Passed	Passed	Passed		
	Aluminum	0/25	-----	-----	-----	-----	-----
		Passed					
10	Gold	0/25	-----	-----	-----	-----	-----
		Passed					
	Gold	0/25	-----	-----	-----	-----	-----
		Passed					
15	Nickel	0/25	-----	-----	-----	-----	-----
		Passed					
	Nickel	0/25	-----	-----	-----	-----	-----
20		Passed					

a) Sample not evaluated.

b) Tape rating in lb. for 1/2 inch wide tape.

Example 16

STPCDP resin of Example 5 was dissolved in toluene to yield a solution of composition 47.2% STPCDP and 52.8% toluene. This solution was spin coated onto an alumina or silicon substrate (surface) utilizing spin coating rate of 1000 rpm for 60 seconds; soft baked for 1 hour at 60°C under nitrogen. The polymer was hard baked employing a cure cycle under nitrogen of 25°C to 220°C ramp in 3 hour, held at 220°C for 2.0 hours and then ramped from 220°C to 25°C in 4 hours.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal shock cycling. A thermal shock cycle encompasses the following thermal cycling of the sample: hold at -55°C

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for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes.

<u>Adhesion Measurements Results</u>				
Substrate	Before Thermal		After 92 Cycles	
	<u>Shock Cycling</u>			
5	2.5	10.0	2.5	10.0
	1b.	1b.	1b.	1b.
Alumina	25/25	25/25	25/25	25/25
10	Passed	Passed	Passed	Passed
Silicon	25/25	25/25	25/25	25/25
	Passed	Passed	Passed	Passed

#### Example 17

15 STPCDP resin of Example 5 was dissolved in toluene to yield a solution of composition 47.2% STPCDP and 52.8% toluene. This solution was spin coated onto an alumina substrate (surface) onto which had been ion-sputtered with a metal film of thickness 5000Å, 20 utilizing spin coating rate of 1000 rpm for 60 seconds; soft baked for 1 hour at 60°C under nitrogen. The polymer was hard baked employing a cure cycle under nitrogen of 25°C to 220°C ramp in 3 hours, held at 220°C for 2.0 hours and then ramped from 220°C to 25°C 25 in 4 hours.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal shock cycling. A thermal shock cycle encompasses the following thermal cycling of the sample: hold at -55°C 30 for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes.

<u>Adhesion Measurements Results</u>				
	Metal	Before Thermal		After 92 cycles
	<u>Layer</u>	<u>Shock Cycling</u>		<u>                    </u>
35		<u>2.5 lb</u>	<u>10.0 lb</u>	<u>2.5 lb. 10.0 lb</u>
	Chromium	25/25	25/25	25/25 25/25
		Passed	Passed	Passed Passed

5	Nickel	25/25	25/25	25/25	25/25
		Passed	Passed	Pass d	Passed
	Copper	25/25	25/25	25/25	25/25
		Passed	Passed	Passed	Passed
	Aluminum	25/25	25/25	a	a
10		Passed	Passed		
	Gold	25/25	25/25	25/25	25/25
		Passed	Passed	Passed	Passed
	a) Sample not evaluated.				

It can be seen in the above Examples 13-15 that chromium adhered particularly well to the dielectric polymers and thus can serve as a suitable base for copper layers which provide conductive patterns in the multilevel structures.

#### Example 18

##### Preparation of crosslinked polymer; thermal curing.

The styrene terminated para-cresol dicyclopentadiene (STPCDP) and styrene terminated tetraphenol ethane (STTPE) prepared as described in Examples 4 and 9, respectively, were thermally cured using the following cure cycle: 2 hours at 80°C, 100°C for 16 hours, 120°C for 4 hours, 160°C for 16 hours, 200°C for 2 hours, and 225°C for 1 hour. Some properties of the resulting cured mixed resins are summarized in the following table.

Table A

30	<u>SAMPLE NO.</u>	1	2	3
		(90/10)	(75/25)	(50/50)
	<u>STPCDP/STTPE</u>			
	T <sub>g</sub> (°C) <sup>(a)</sup>	>300	>300	>300
35	T <sub>sp</sub> (°C) <sup>(b)</sup>	147±3	160±4	161±2
	α <sub>sp</sub> (ppm/°C) <sup>(c)</sup>	75±3	70±9	74±2

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	$\alpha_{260}$ (ppm/°C) <sup>(d)</sup>	167±1	110±14	93±2
	$\epsilon'$ <sup>(e)</sup>	2.75	2.79	2.77
	$\tan \delta$ <sup>(f)</sup>	0.0003	0.0005	0.003
5	$\epsilon'$ <sup>(g)</sup>	2.76	2.85	2.77
	$\tan \delta$ <sup>(h)</sup>	0.002	0.001	0.0008
10	% Water Absorption <sup>(i)</sup>	0.102	0.110	0.136
	Modulus (GPa) <sup>(j)</sup>	9.1	9.2	8.9
15	Tg (°C) <sup>(k)</sup>	>200	>200	>200
	(a) glass transition temperature by differential scanning calorimeter			
	(b) softening point by Thermo Mechanical Analysis - minor thermal transition			
20	(c) coefficient of thermal expansion between 25°C and softening point			
	(d) coefficient of thermal expansion between 25°C and 260°C			
	(e) dielectric constant at 1 MHz and 0% Relative Humidity at 25°C			
25	(f) loss tangent at 1 MHz and 0% Relative Humidity at 25°C			
	(g) dielectric constant at 1 MHz and 50% Relative Humidity at 25°C			
30	(h) loss tangent at 1 MHz and 50% Relative Humidity at 25°C			
	(i) at 50% Relative Humidity, 25°C for 168 hours			
	(j) modulus measured from -125°C to 200°C at 4 Hz			
35	(k) glass transition temperature by DMA at 4 Hz range scanned -125°C to 200°C			

Example 19

A series of coating solutions were prepared and used to coat silicon surfaces. The solution

concentrations were between 50.8 and 53.1 wt. % STPCDP (Example 5) and STTPE (in Example 9) in toluene. The solutions were applied by spin coating at 900-950 rpm for 60 seconds. The coated discs were soft baked at 25°C for 18 hours under vacuum. Then, they were exposed for 3 minutes to UV irradiation with a 300 watt mercury vapor lamp with a quartz/water filter. The irradiated coatings were then exposed to various solvents and the amount of cured resin dissolved was measured. The results are shown in the following tables.

Table B  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:Ethanol)<sup>(b)</sup>

<u>Time(sec)</u>	<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
0	0	0	0	0	0	0
30	3.59	6.29	11.30	9.42	26.98	0.34
60	2.99	7.86	12.62	11.69	30.16	0.00
90	6.29	10.38	13.95	14.94	34.60	2.03
120	6.59	10.69	15.28	16.56	35.24	2.03
180	8.08	11.32	16.28	16.56	35.24	1.69
300	5.39	9.12	15.61	17.86	34.92	0.68

a) 90 STPCDP/10 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.

b) Weight % solutions.

Table C  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:n-Hexane)<sup>(b)</sup>

<u>Time(sec)</u>	<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
0	0	0	0	0	0	0

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	30	3.59	-1.71	-2.76	0.36	0.34	-0.66
	60	2.99	-1.71	5.17	2.87	-0.67	-2.32
	90	6.29	-2.05	15.17	8.24	2.69	-0.33
	120	6.59	-1.71	18.62	15.41	6.73	-0.66
5	180	8.08	-2.05	21.38	23.66	14.81	0.00
	300	5.39	-3.07	24.83	28.32	25.25	1.99

- a) 90 STPCDP/10 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.
- b) Weight % solutions.

Tables B and C may be compared with the results of Tables D and E below in which only the soft bake was carried out and no curing by UV radiation was done.

Table D

% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:Ethanol)<sup>(b)</sup>

20	<u>Time(sec)</u>	<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
	0	0	0	0	0	0	0
	30	99.08	99.32	100.00	41.55	96.92	1.72
	60	98.16	98.98	99.34	53.72	99.32	1.03
25	90	100.61	100.68	101.97	71.28	100.34	1.37
	120	99.69	101.36	100.99	73.31	100.00	2.06
	180	100.92	100.68	100.00	77.70	100.68	2.41
	300	99.69	100.34	100.33	79.05	99.32	2.41

- a) 90 STPCDP/10 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs.
- b) Weight % solutions.

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Table E  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:n-Hexane)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
5	0	0	0	0	0	0	0
	30	99.08	102.14	13.57	-3.03	1.69	-0.70
	60	98.16	101.42	91.79	30.64	-1.36	-1.75
	90	100.61	101.07	98.57	78.11	8.81	-1.05
	120	99.69	102.49	98.57	95.62	29.83	0.35
10	180	100.92	101.42	99.64	97.31	62.03	0.70
	300	99.69	101.78	100.00	99.66	76.95	3.15

- a) 90 STPCDP/10 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs.
- b) Weight % solutions.

Table F  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:Ethanol)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
20	0	0	0	0	0	0	0
	30	53.97	64.84	64.38	20.00	-2.05	0.00
	60	69.21	70.33	70.21	30.36	-2.05	-1.39
	90	70.86	73.63	70.89	37.50	-0.68	-1.39
	120	71.85	71.79	71.58	42.50	-1.02	0.63
25	180	71.85	74.36	72.95	45.36	-1.37	0.35
	300	74.83	74.73	73.29	50.71	0.34	0.35

- a) 75 STPCDP/25 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.
- b) Weight % solutions.

Table G  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:n-Hexane)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
5							
	0	0	0	0	0	0	0
	30	53.97	69.47	0.73	-1.10	1.01	-0.70
	60	69.21	73.33	18.18	8.46	-0.34	-1.76
	90	70.86	77.89	42.55	30.15	0.34	-2.82
10	120	71.85	78.25	48.73	41.54	1.35	-1.41
	180	71.85	78.25	52.36	51.84	3.03	-1.06
	300	74.83	81.40	54.55	60.29	6.40	-1.76

15 a) 75 STPCDP/25 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.

b) Weight % solutions.

20 Tables F and G may be compared with the results of Tables H and I below in which only a soft bake was carried out and no curing by UV radiation was done.

Table H  
% STPCDP/STTPE<sup>(a)</sup> Removed  
Solvent (Toluene:Ethanol)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
25							
	0	0	0	0	0	0	0
	30	96.10	98.98	89.66	28.09	0.68	2.42
30	60	99.29	101.36	98.62	47.16	3.74	2.42
	90	99.65	99.66	99.66	57.53	5.78	1.04
	120	99.65	100.34	100.00	64.55	6.12	2.08
	180	99.29	99.32	99.31	69.90	9.18	2.08
	300	100.35	100.34	99.31	75.25	10.88	1.38

35

- a) 75 STPCDP/25 STTPE coated on silicon wafer and soft baked at 25°C for 18 hrs.
- b) Weight % solutions.

Table I

5                    % STPCDP/STTPE<sup>(a)</sup> Removed  
                      Solvent (Toluene:n-Hexane)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
10	0	0	0	0	0	0	0
	30	96.10	59.52	-2.00	-5.35	-0.33	1.00
	60	99.29	98.96	54.00	10.37	-3.92	1.00
	90	99.65	99.65	85.00	46.82	3.92	0.33
	120	99.65	100.35	95.00	74.25	7.52	0.33
15	180	99.29	99.65	98.67	87.96	16.99	0.33
	300	100.35	100.35	99.00	95.99	35.62	0.33

- a) 75 STPCDP/25 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs.
- b) Weight % solutions.

20

Table J

% STPCDP/STTPE<sup>(a)</sup> Removed  
                      Solvent (Toluene:Ethanol)<sup>(b)</sup>

<u>Time(sec)</u>		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
25	0	0	0	0	0	0	0
	30	2.56	10.84	3.73	-2.69	-2.60	-1.86
	60	3.66	15.38	10.45	-0.38	-1.49	-1.12
	90	7.69	17.83	14.18	3.85	-2.97	0.00
	120	12.09	18.53	18.66	3.85	-0.74	-1.12
30	180	13.19	20.98	18.66	6.54	-0.37	1.86
	300	14.65	23.08	27.99	11.54	10.04	0.00

- a) 50 STPCDP/50 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute
- 35                    cure 300 Watt Mercury Vapor Lamp with quartz/water filter.

b) Weight % solutions.

Table K

% STPCDP/STTPE<sup>(a)</sup> Removed

Solvent (Toluene:n-Hexane)<sup>(b)</sup>

5	<u>Time(sec)</u>						
		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
	0	0	0	0	0	0	0
	30	2.56	1.13	0.00	-0.39	0.00	-0.37
	60	3.66	2.26	1.84	2.33	1.57	0.00
10	90	7.69	3.02	1.84	-0.39	0.39	0.00
	120	12.09	3.40	2.94	1.95	1.18	0.00
	180	13.19	7.55	2.94	1.95	0.78	0.00
	300	14.65	10.94	2.94	3.11	3.14	0.00

15 a) 50 STPCDP/50 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs., 3 minute cure 300 Watt Mercury Vapor Lamp with quartz/water filter.

b) Weight % solutions.

20

Table J and K may be compared with the results of Tables L and M below in which only the soft bake was carried out and no curing by UV radiation was done.

Table L

% STPCDP/STTPE<sup>(a)</sup> Removed

Solvent (Toluene:Ethanol)<sup>(b)</sup>

25	<u>Time(sec)</u>						
		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
	0	0	0	0	0	0	0
30	30	97.03	102.24	95.47	37.36	-1.57	-2.14
	60	100.74	99.63	98.87	65.66	3.54	0.00
	90	101.12	99.63	99.62	73.58	5.12	-0.71
	120	100.37	99.25	99.25	80.75	7.48	-1.42
	180	101.12	98.88	98.11	83.40	10.24	-3.20
35	300	101.12	98.88	101.13	87.55	15.75	-0.71

- a) 50 STPCDP/50 STTPE coated on silicon wafer and soft baked at 25°C for 18 hrs.
- b) Weight % solutions.

5

Table M% STPCDP/STTPE<sup>(a)</sup> RemovedSolvent (Toluene:n-Hexane)<sup>(b)</sup>Time(sec)

		<u>100:0</u>	<u>80:20</u>	<u>60:40</u>	<u>40:60</u>	<u>20:80</u>	<u>0:100</u>
10	0	0	0	0	0	0	0
	30	97.03	99.25	-3.18	-3.04	0.35	-0.71
	60	100.74	103.02	39.93	-0.38	0.70	-1.79
	90	101.12	101.51	91.87	14.45	5.61	-0.71
	120	100.37	102.64	98.94	56.27	12.98	0.00
15	180	101.12	104.15	98.23	80.23	20.70	0.00
	300	101.12	103.77	99.29	92.02	35.09	-0.36

- a) 50 STPCDP/50 STTPE by weight coated on silicon wafer and soft baked at 25°C for 18 hrs.
- 20 b) Weight % solutions.

Example 20

A series of 50% STPCDP (Example 6) and 50% STTPE (Example 9) solutions were prepared in toluene were prepared at different concentrations ranging from

25 46.0 Wt. % solids to 58.4 Wt. % solids. These solutions were spin coated onto a silicon substrate (surface) utilizing spin coating rates from 700 rpm to 1500 rpm for 60 seconds; soft baked for 24 hours at 25°C under vacuum. The samples were then exposed for

30 3 minutes to UV irradiation with a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The air dried substrate was hard baked employing a cure cycle under vacuum of

35 25°C to 220°C ramp in 1 hour, held at 220°C for 2.5 hours and then cooled to room temperature.

The film thickness of the photocured polymer was analyzed employing a Taylor-Hobson Talysurf 10 profilometer. The following table illustrates the film thicknesses obtained.

5

Table N

			<u>Film Thickness (<math>\mu\text{m}</math>)</u>		
50 STPCDP/50 STTPE Viscosity Spin Coating Speed (rpm)					
<u>Solids Content<sup>(a)</sup></u>	<u>(mPa s)</u>		<u>700</u>	<u>1000</u>	<u>1500</u>
10 46.0	6.0		5.3	4.4	4.2
48.9	10.0		7.5	6.3	4.7
53.5	16.0		10.5	8.2	6.8
58.4	32.0		----	12.9	10.9

15 a) Dissolved solids content in Toluene

Example 21

A 56 Wt. % solids solution of 50% STPCDP, 50% STTPE solution was prepared in toluene using of STPCDP of Example 6 and STTPE of Example 9. This solution was spin coated onto a silicon substrate (surface) utilizing spin coating rates from 600 rpm to 2000 rpm for 60 seconds; soft baked for 24 hours at 25°C under vacuum. The samples were then exposed for 3 minutes to UV irradiation with a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The air dried substrate was hard baked employing a cure cycle under vacuum of 25°C to 219°C ramp in 1 hour, held at 219°C for 2.5 hours and then cooled to room temperature.

The film thickness and sidewall angle of the photocured polymer was analyzed utilizing a Sloan Technology Corporation Dektak 3030 profilometer. This data is summarized in the following table.

5	<u>Table G</u>		
	Spin Speed (rpm)	Film thickness ( $\mu\text{m}$ )	Sidewall Angle
10	600	13.5	19
	600	13.5	20
	700	12.0	35
	700	12.0	30
	800	12.3	33
15	800	11.2	21
	800	11.3	35
	800	12.0	18
	1000	10.3	24
	1000	10.5	28
20	1000	10.0	33
	1000	11.2	26
	1500	8.5	22
	1500	8.8	30
	1500	9.2	26
25	1500	12.4	18
	2000	7.5	25
	2000	7.7	9
	2000	7.9	37
	2000	8.0	20

30

Example 22

A series of 50% STPCDP (Example 6) and 50% STTPE (Example 9) solutions were prepared in toluene were prepared at different concentrations ranging from 46.0 Wt. % solids to 58.4 Wt. % solids. These solutions were spin coated onto a silicon substrate (surface) utilizing spin coating rates from 700 rpm to

1500 rpm for 60 seconds; soft baked for 24 hours at 25°C under vacuum. The samples were then exposed for 3 minutes to UV irradiation with a 300 watt mercury lamp employing an USAF Test Pattern and a quartz/water  
 5 filter. The photocured polymer was then developed with toluene for 1 minute at 25°C. The air dried substrate was hard baked employing a cure cycle under vacuum of 25°C to 220°C ramp in 1 hour, held at 220°C for 2.5 hours and then cooled to room temperature. The samples  
 10 were then metallized via ion-beam sputtering to yield a metal film of thickness 5000 to 10000 Å.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal shock cycling. A thermal shock cycle encompasses the  
 15 following thermal cycling of the sample: hold at -55°C for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes. In the following tables the ratio given means that of 25 squares of the metal, some to all of them were not removed by the tape. That is,  
 20 5/25 means that 20 squares of metal were removed.

#### Adhesion Measurements Results

		Metal Before Thermal		After 92 Cycles		After 184 Cycles	
		<u>Layer Shock Cycling</u>					
25		2.5	10.0	2.5	10.0	2.5	10.0
		<u>lb. (b)</u>	<u>lb.</u>	<u>lb.</u>	<u>lb.</u>	<u>lb.</u>	<u>lb.</u>
	Chromium	0/25	---	---	---	---	---
30		Passed					
	Chromium	0/25	---	---	---	---	---
		Passed					
35	Copper	0/25	---	---	---	---	---
		Passed					

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	Copper	0/25	---	---	---	---	---
		Passed					
5	Aluminum	1/25	0/1	---	---	---	---
		Passed	Passed				
	Aluminum	0/25	---	---	---	---	---
		Passed					
10	Gold	6/25	6/6	a	a	a	a
		Passed	Passed				
	Gold	0/25	---	---	---	---	---
		Passed					
15	Nickel	0/25	---	---	---	---	---
		Passed					
	Nickel	0/25	---	---	---	---	---
20		Passed					
	a) Sample not evaluated.						
	b) Tape rating in lb for 1/2 inch wide tape						

Example 23

STPCDP resin of Example 5 and STTPE of Example 9 was dissolved in toluene to yield a solution of (50:50 STPCDP:STTPE) composition 28.0 Wt.% STPCDP, 28.0 Wt.% STTPE and 44 Wt.% toluene. This solution was spin coated onto an alumina or silicon substrate (surface) utilizing spin coating rate of 1000 rpm for 60 seconds; soft baked for 1 hour at 60°C under nitrogen. The polymer was hard baked employing a cure cycle under nitrogen of 25°C to 220°C ramp in 3 hour, held at 220°C for 2.0 hours and then ramped from 220°C to 25°C in 4 hours.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal

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shock cycling. A thermal shock cycle encompasses the following thermal cycling of the sample: hold at -55°C for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes.

5		<u>Adhesion Measurements Results</u>			
	<u>Substrate</u>	<u>Before Thermal Shock Cycling</u>		<u>After 92 Cycles</u>	
		<u>2.5 lb.</u>	<u>10.0 lb.</u>	<u>2.5 lb.</u>	<u>10.0 lb.</u>
0	Alumina	0/25 Passed	----	----	----
	Silicon	0/25 Passed	----	----	----

#### Example 24

STPCDP resin of Example 5 and STTPE of Example 9 was dissolved in toluene to yield a solution of (50:50 STPCDP:STTPE) composition 28.0 Wt.% STPCDP, 28 Wt.% STTPE and 44 Wt.% toluene. This solution was spin coated onto an alumina substrate (surface) onto which had been ion-sputtered with a metal film of thickness 5000Å, utilizing spin coating rate of 1000 rpm for 60 seconds; soft baked for 1 hour at 60°C under nitrogen. The polymer was hard baked employing a cure cycle under nitrogen of 25°C to 220°C ramp in 3 hours, held at 220°C for 2.0 hours and then ramped from 220°C to 25°C in 4 hours.

The adhesion was evaluated via a calibrated "Scotch-Tape" adhesion test before and after thermal shock cycling. A thermal shock cycle encompasses the following thermal cycling of the sample: hold at -55°C for 10 minutes, -55°C to 125°C over a rapid ramp, hold at 125°C for 10 minutes.

		<u>Adhesion Measurements Results</u>			
	<u>Metal Layer</u>	<u>Before Thermal</u>		<u>After 92 Cycles</u>	
		<u>Shock Cycling</u>			
		<u>2.5 lb</u>	<u>10.0 lb</u>	<u>2.5 lb.</u>	<u>10.0 lb</u>
5	Chromium	25/25 Passed	25/25 Passed	a	a
10	Nickel	0/25 Passed(b)	----	----	----
	Copper	0/25 Passed(b)	----	----	----
	Aluminum	0/25 Passed(b)	----	----	----
15	Gold	0/25 Passed(b)	----	----	----

a) Sample not evaluated.

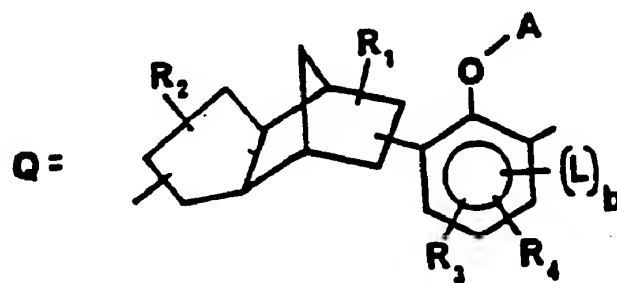
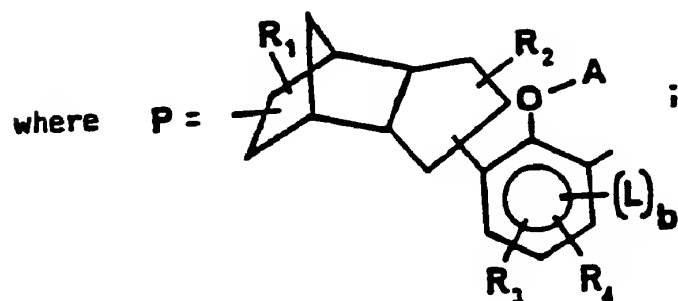
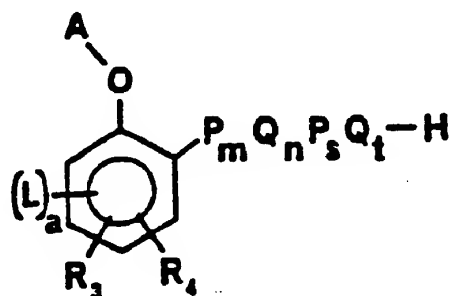
b) Failed at polymer to metal interface.

- 20 It can be seen in the above Examples 22-24 that chromium adhered particularly well to the dielectric polymers and thus can serve as a suitable base for copper layers which provide conductive patterns in the multilevel structures.

CLAIMS:

1. A method of forming a polymer on a substrate in a predetermined pattern comprising:

(a) coating a substrate with a prepolymer which is an ether of the reaction product of dicyclopentadiene with phenol having the formula




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with  $R_1, R_2 = H$  or alkyl of 1-10 carbon atoms;

$R_3 = \text{methyl}$ ;

$R_4 = H$ ;

$A = H, -CH_2 -$   , an alkyl moiety containing 1

to 10 carbon atoms,  $R_5$  a cycloalkyl moiety having 5 to 10 carbon atoms, or benzyl, subject to the constraint that at least 50% of all A's are the vinyl benzyl moiety;

$L = Br$  or  $Cl$ ;

$a = 0, 1, \text{ or } 2$ ;

$b = 0$  or  $1$ ;

$m, n, s,$  and  $t$  are 0 or an integer, and  $m+n+s+t=z$  is an integer from 1-10; and

$R_5 = H$ , an alkyl moiety of 1-10 carbon atoms, a halogen or alkoxy moiety, or a monovalent aromatic radical.

(b) irradiating the coated prepolymer of (a) through a masking pattern to selectively crosslink the portion of said coating being irradiated;

(c) selectively dissolving the non-irradiated part of the prepolymer coating of (a); and

(d) curing the crosslinked portion of the prepolymer coating by heating at a temperature in the range of  $100^\circ C$  to  $300^\circ C$  for a time sufficient to further crosslink said crosslinked coating and to transform the prepolymer to an infusible glassy solid.

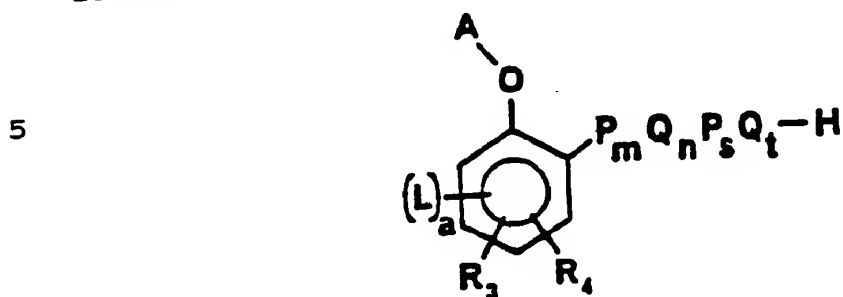
2. A method of forming a polymer on a substrate in a predetermined pattern comprising:

(a) coating a substrate with a mixture of prepolymers which comprises

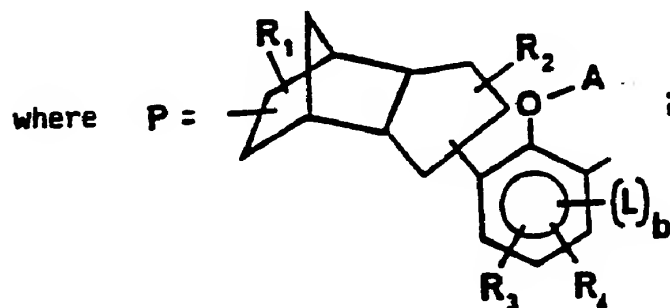
(1) an ether of the reaction product of

60

dicyclopentadiene with phenol having the formula

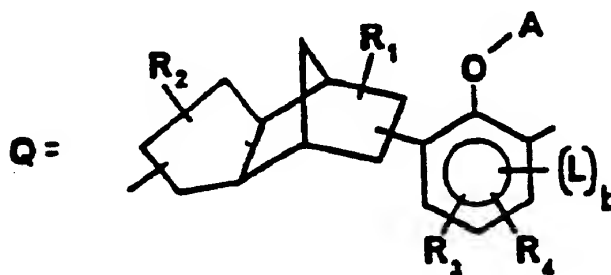


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15

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25

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with  $R_1, R_2 = H$  or alkyl of 1-10 carbon atoms;

$R_3 = \text{methyl};$

$R_4 = H;$

35  $A = H, -CH_2 -$  , an alkyl moiety containing 1

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to 10 carbon atoms, a cycloalkyl moiety having 5 to 10 carbon atoms, or benzyl;

L = Br or Cl;

a = 0, 1, or 2;

5 b = 0 or 1;

m, n, s, and t are 0 or an integer, and  $m+n+s+t=z$  is an integer from 1-10; and

10  $R_5$  = H, an alkyl moiety of 1-10 carbon atoms, a halogen or alkoxy moiety, or a monovalent aromatic radical.

(2) an ether of the oligomeric condensation product of

a) molar proportion of a dialdehyde and

15 b) from about 3 to about 4 molar proportions of a phenol; when the dialdehyde is selected from the group consisting of  $\text{OHC}(\text{CH}_2)_r\text{CHO}$ , where  $r = 0$  or an integer from 1 to 6, cyclopentanedialdehyde, phthalaldehyde, isophthalaldehyde, terephthalaldehyde, hexahydrophthalaldehyde, cycloheptanedi-  
20 aldehyde, hexahydroisophthalaldehyde, hexahydroterephthalaldehyde, and cyclooctanedialdehyde;

25 where the phenol has the structure  $R_6\text{C}_6\text{H}_4$  and  $R_6$  is hydrogen or an alkyl group containing from 1 to about 10 carbon atoms; and where the phenol residue of said oligomeric condensation product is etherified with one  
30 or more substituents to afford ether moieties randomly selected from the group consisting of vinylbenzyl, alkyl moieties containing from 1 to 10 carbon atoms, cycloalkyl moieties from 5 to 10 carbon atoms, and  
35 benzyl, with the ratio of vinylbenzyl to other moieties being from 1:1 to about 6:1;

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- (b) irradiating the coated prepolymer of (a) through a masking pattern to selectively crosslink the portion of said coating being irradiated;
- 5 (c) selectively dissolving the non-irradiated part of the prepolymer coating of (a); and
- (d) curing the crosslinked portion of the prepolymer coating by heating at a temperature in the range of 100° to 300°C for a time sufficient to further crosslink said crosslinked coating and to transform the prepolymer to an infusible glassy solid.
- 10 3. The method of Claims 1 or 2 wherein R<sub>1</sub> and R<sub>2</sub> are hydrogen.
- 15 4. The method of Claims 1 or 2 wherein Z is 3 or 4.
5. The method of Claims 1 or 2 wherein A is para vinyl benzyl.
6. The method of Claims 1 or 2 wherein L is Br.
7. The method of Claims 1 or 2 wherein 70% of A is vinyl benzyl and the remainder is propyl.
- 20 8. The method of Claim 2 wherein the dialdehyde is OHC(CH<sub>2</sub>)<sub>r</sub>CHO and r is 0 or an integer from 1 to 6.
9. The method of Claim 2 wherein R<sub>6</sub> is hydrogen or methyl.
- 25 10. The method of Claim 2 wherein the ether moieties of the condensation product (2) are about 70% vinyl benzyl and 30% propyl.
11. The method of Claim 2 wherein the molecular weight of condensation product (2) is 400 to 6000.
- 30 12. An electronic interconnect structure comprising the cured polymer prepared by the method of Claims 1 or 2.
13. An electronic interconnect structure of Claim 12 wherein said cured polymer is adhered to a layer of chromium metal.
- 35



# INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/09392

<b>I. CLASSIFICATION OF SUBJECT MATTER</b> (If several classification symbols apply, indicate all) * According to International Patent Classification (IPC) or to both National Classification and IPC IPC <sup>5</sup> : G 03 F 7/11, H 01 B 3/36, C 07 C 42/20		
<b>II. FIELDS SEARCHED</b> Minimum Documentation Searched * Classification System   Classification Symbols IPC <sup>5</sup>   G 03 F 7/00, H 01 B 3/00, C 07 C 42/00 Documentation Searched other than Minimum Documentation to the Extent that such Documents are Included in the Fields Searched *		
<b>III. DOCUMENTS CONSIDERED TO BE RELEVANT</b> *		
Category *	Citation of Document, ** with indication, where appropriate, of the relevant passages **	Relevant to Claim No. **
Y	WO, A1, 89/12 846 (ALLIED-SIGNAL) 28 December 1989 (28.12.89), see claim 1.	1
Y	US, A, 4 540 829 (HEFNER) 10 September 1985 (10.09.85), see claim 1.	1
X	US, A, 4 824 920 (RUFANCIC) 25 April 1989 (25.04.89), see claims 1-28.	1
A	CHEMICAL ABSTRACTS, vol. 101, no. 9, issued 1984, August 27, (Columbus, Ohio, USA), ALAN P. MARCHAND et al. "Stereochemistry of the re- action of 7-substituted norbornadienes with iron	1
* Special categories of cited documents: ** - "A" document defining the general state of the art which is not considered to be of particular relevance - "E" earlier document but published on or after the international filing date - "L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified) - "O" document referring to an oral disclosure, use, exhibition or other means - "P" document published prior to the international filing date but later than the priority date claimed - "T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention - "X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step - "Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such docu- ments, such combination being obvious to a person skilled in the art - "Z" document member of the same patent family		
<b>IV. CERTIFICATION</b>		
Date of the Actual Completion of the International Search 02 April 1992		Date of Mailing of this International Search Report 15 APR 1992
International Searching Authority EUROPEAN PATENT OFFICE		Signature of Authorized Officer Mme N. KUIPER

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, " with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	carbonyls. 2. Reaction of Fe(CO) <sub>5</sub> with 7-phenyl- and 7-o-anisylbornadiene.", see page 577, column 1, the abstract-no. 71 894j, & J. Org. Chem. 1984, 49(16), 2897-900 (Eng). --	
A	CHEMICAL ABSTRACTS, vol. 61, no. 2, issued 1964, July 20, (Columbus, Ohio, USA), L.A. KHEIFITS et al. "Terpenylphenols. XVII. Condensation of 1,4,5,8-bis(endomethylene)octahydronaphthalene with phenol and further transformations of the products of condensation)", see column 1774, the abstract-no. 1 774f, & Zh. Obshch. Khim. 34(4), 1208-11(1964). --	1
A	CHEMICAL ABSTRACTS, vol. 61, no. 8, issued 1964, October 12, (Columbus, Ohio, USA), R.I. SHARAPOVA et al. "Spectrophotometric determination of ortho and para isomers of certain alkyl and terpene phenols.", see column 8897, the abstract-no. 8 897d, & Zh. Analit. Khim. 19(6), 771-4(1964). --	1
A	CHEMICAL ABSTRACTS, vol. 101, no. 2, issued 1984, July 9, (Columbus, Ohio, USA), HITACHI CHEMICAL CO., LTD., "Photosensitive resin compositions.", see page 495, column 1, the abstract-no. 15 031p, & Jpn. Kokai Tokkyo Koho JP 58,163,937. --	1
A	CHEMICAL ABSTRACTS, vol. 107, no. 26, issued 1987, December 28, (Columbus, Ohio, USA), ISHIO, NORIAKI et al.	1

III. DOCUMENTS CONSIDERED TO BE RELEVANT (CONTINUED FROM THE SECOND SHEET)		
Category *	Citation of Document, * with indication, where appropriate, of the relevant passages	Relevant to Claim No.
	<p>"Patterning using graft co-polymerization process.", see page 671, column 2, the abstract-no. 246 734k, &amp; Jpn. Kokai Tokkyo Koho JP 62,168,134. -----</p>	

# ANHANG

\* zum internationalen Recherchen-  
bericht über die internationale  
Patentanmeldung Nr.

# ANNEX

to the International Search  
Report to the International Patent  
Application No.

# ANNEXE

au rapport de recherche inter-  
national relatif à la demande de brevet  
international n°

PCT/US 91/09392 SAE 55507

In diesem Anhang sind die Mitglieder  
der Patentfamilien der im obenge-  
nannten internationalen Recherchenbericht  
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